PB82-234105

Technical Basis for Developing Control Strategies for High Ambient Concentrations of Nitrogen Dioxide

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Sep 80

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/4-80-017
September 1980

Air

PB82-234105

EPA

Technical Basis for Developing Control Strategies for High Ambient Concentrations of Nitrogen Dioxide

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-450/4-80-017	2.	3. RECIPIENT'S ACCESSION NO. PB82 234105
4. TITLE AND SUBTITLE Technical Basis for Developing Control Strategies for High Ambient Concentrations of Nitrogen Dioxide		5. REPORT DATE September 1980
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Edwin L. Meyer, Donald H. Sennet, Henry S. Cole and Harold G. Richter		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U. S. Environmental Protection Agency Office of Air Quality Planning and Standards Monitoring and Data Analysis Division (MD-14) Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

Report presents information which may prove useful in designing control strategies to reduce high short-term and/or annual concentrations of nitrogen dioxide (NO_2). Specific implications of findings of the design of control strategies are identified. The following topics are discussed: (1) nature and significance of manmade and natural sources of NO_x; (2) mechanisms by which NO_2 is formed in the atmosphere; (3) monitoring network design, data quality checks, and the extent of high NO_2 concentrations observed in the U.S. from 1975-77; (4) the extent to which NO_2 is transported from urban to suburban areas and over longer distances; (5) derived relationships between NO_2, NO and organic pollutants; (6) procedures for examining monitoring data to estimate impacts of various source categories observed on high levels of NO_2; and (7) modeling procedures for NO_2 which are available.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Nitrogen Dioxide Air Quality Management Photochemical Pollutants Air Pollution Control Strategies		
18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 145
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

TECHNICAL BASIS FOR DEVELOPING CONTROL STRATEGIES FOR HIGH AMBIENT CONCENTRATIONS OF NITROGEN DIOXIDE

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Monitoring and Data Analysis Division
Research Triangle Park, North Carolina

September 1980

This document is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current EPA contractors and grantees, and nonprofit organizations - in limited quantities - from the Library Services Office (MD-35), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711; or, for a fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

This document has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and approved for publication. Subject to clarification, the contents reflect current Agency thinking.

Publication No. EPA-450/4-80-017

TABLE OF CONTENTS

Page

List of Tables v

List of Figures vi

Executive Summary ix

1.0 Introduction 1

2.0 Emissions of NO_x 3

2.1 Anthropogenic Emissions 3

2.2 Natural Sources of NO_x 6

2.3 Significance of Manmade Versus Natural Emissions 6

2.4 Implications 7

3.0 Mechanisms for NO_2 Formation in the Atmosphere 10

3.1 Photochemical Synthesis of Nitrogen Dioxide 11

3.2 Titration 13

3.3 Carryover 18

3.4 Implications 20

4.0 Monitoring, Data Quality and the Observed Extent of High NO_2 Concentrations 22

4.1 Network Design and Operation 22

4.2 Data Quality Assurance Techniques 25

4.3 NO_2 Concentrations Observed in Excess of 0.20 ppm 26

4.4 Implications 31

5.0 Transport of NO_2 34

5.1 Urban Gradients of NO_2 34

5.2 Levels of NO_2 Reported in Rural Areas 43

5.3 Chemistry of Transported NO_x 46

5.4 Implications 51

Table of Contents (continued)

Page

6.0 Relationships Between NO_2 and its Precursors 53
  6.1 Relations Among NO_2 and Precursors 53
    6.1.1 Smog Chamber Experiements 54
    6.1.2 Empirical Relationships from Ambient Data 58
    6.1.3 Relationships Derived from Chemical Kinetics Models 62
  6.2 Implications 67
7.0 Impact of Controlling Various Source Categories 71
  7.1 Tracer Approaches 73
  7.2 Use of Peak-to-Mean Ratios 76
  7.3 Impact of Point Sources on Ambient Levels of NO_2 80
  7.4 Implications 95
8.0 Use of Models for NO_2 99
  8.1 Multisource Urban Models 100
    8.1.1 Linear Rollback 100
    8.1.2 OZIPM 108
    8.1.3 Photochemical Box Model (PBM) 110
    8.1.4 Complex Multisource Models. 112
  8.2 Models to Assess the Impact from Individual Sources. . . . 112
  8.3 Implications 122
9.0 References. 127
10.0 Acknowledgement 131

LIST OF TABLES

Number		Page
2.1	1977 National NO_x Emissions by Source Category (Expressed as NO_2)	5
2.2	NO_x Emissions in Selected Urban Counties*.	8
4.1	Distribution of NO_2 Concentration $\geq$ 0.20 ppm for all California Monitoring Stations, 1975-1977*	30
5.1	High NO_2 Values Observed in the Vicinity of Los Angeles, 1975-1977	36
5.2	Spatial Distribution of Hourly NO_2 Concentrations in the RAPS Network, 1976	41
5.3	NO_2 Observed at Rural Sites	44
5.4	Concentration of Nitrogen Oxides Observed in Clean Remote Areas	45
5.5	Chemical Stability of NO_x Corresponding to Observed Conversation Rates	48
6.1	Summary of Conclusions from Smog Chamber Experiments . .	57
6.2	Empirically Estimated Dependence of NO_2 on NO_x Control .	60
6.3	Estimated Impact of Reducing NMOC on Peak NO_2 Obtained with Empirical Models	61
6.4	Effect of Separate NO_x and NMOC Reductions on Peak NO_2 Under Various Conditions*.	63
8.1	Sensitivity of Peak NO_2 to Changes in NMOC with Various Prevailing NMOC/NO_x Ratios	104
8.2	Available Complex Multisource Photochemical Dispersion Models	113
8.3	Approaches for Estimating Maximum Impact on Peak NO_2 from Large Individual Sources	117
8.4	Hypothetical Example Illustrating Use of Multi and Individual Source Models for Projecting Future Short Term NO_2 Concentrations for Use in SIP's	123

LIST OF FIGURES

Number — Page

3.1 Illustration of Photochemical and Titration Formation of NO_2 12

3.2 Ozone Limiting Case of Titration 16

3.3 NO Limiting Case of Titration. 17

3.4 Diurnal Concentration Profiles Illustrating Carryover. . . 19

4.1 Seasonal Variation in Hourly NO_2 Levels Exceeding 0.20 ppm at all non-California Stations Reporting to SAROAD during 1975-77 27

4.2 Frequency of Maximum 1-hour NO_2 Concentrations $\geq$ 0.20 ppm 28

5.1 Gradients in Maximum hourly NO_2 Observed in the Los Angeles Basin 37

5.2 Example of NO_2 Transport at El Toro Station on January 25, 1975 39

5.3 Pollutant plots for Riverside, October 1-4, 1975 40

5.4 Gradients in Maximum NO_2 Concentrations Observed During the St. Louis RAPS 42

6.1 Nitrogen Dioxide Maximum Concentration versus Initial Oxides of Nitrogen (means of several experiments) UNC Study 55

6.2 Dependence of Nitrogen Dioxide Maximum Concentration on Initial Nitrogen Oxides, Bureau of Mines Study 55

6.3 Maximum one-hour Nitrogen Dioxide Concentration Produced from Irradiation of Multicomponent Hydrocarbon/NO_x Mixtures, General Motors Study 56

6.4 Maximum Nitrogen Dioxide Concentration as a Function of Initial NO_x for Two Initial Hydrocarbon Levels, UC Riverside Study 56

6.5 NO_2, With 8 hours of Emissions and 3%/hr Dilution 64

6.6 NO_2, With 8 hours of Emissions and 10%/hr Dilution 65

List of Figures (continued)   Page

6.7 NO_2, With 10 hours of Emissions and 3%/hr Dilution 66

6.8 NO_2, NO and O_3 Versus Time for Point A (Figure 6.7) . . . 68

6.9 NO_2, NO and O_3 Versus Time for Point B (Figure 6.7) . . . 69

7.1 Pollutant Plots for Lynwood, November 23-25, 1976. 75

7.2 Example of Potential Point Source Impact at Long Beach on Sunday, November 16, 1975 77

7.3 Example of Potential Point Source Impact at Whittier on Monday, August 25, 1975 78

7.4 Dependence of Maximum/mean Ratio on Annual Mean NO_2 Concentrations 81

7.5 Location and Elevation of Clinch River Power Plant Stations 83

7.6 NO_2/NO_x versus NO_x at Clinch River on Days with High NO_x 85

7.7 NO_2 Ratios Observed at Clinch River During Hours with High Ambient NO_x 86

7.8 Evidence of NO_x Aloft Over St. Louis 87

7.9a Horizontal Plume Traverse 21 km Downwind of Labadie Stacks on August 14, 1974 89

7.9b Horizontal Plume Traverse 21 km Downwind of Labadie Stacks on August 14, 1974 90

7.10a Horizontal Plume Traverse 45 km Downwind of Labadie Stacks on August 14, 1974 92

7.10b Horizontal Plume Traverse 45 km Downwind of Labadie Stacks on August 14, 1974 92

7.11 Diagrams for a Titration Reaction in a Turbulent Plume 94

8.1 Conceptual View of the Column Model 109

8.2 Schematic Diagram of Modeling Domain for the Photochemical Box Model 111

List of Figures (continued)

Page

8.3 Nitrogen Dixoide (NO_2) Data from the NO_2/O_3 Sampler Siting Study 115

8.4 Procedure for Applying Rollback in Assessing the Impact of Control Strategies on NO_2 125

EXECUTIVE SUMMARY

This document has two objectives: (1) to provide a concise description of the extent and likely causes of high concentrations of nitrogen dioxide (NO_2), and (2) to identify useful procedures for evaluating the effectiveness of strategies to reduce high concentrations of NO_2. Each chapter reviews one facet of the subject matter. The last section in each chapter summarizes direct implications posed by preceding information.

According to 1977 estimates, over 95 percent of anthropogenic NO_x (i.e., nitric oxide plus nitrogen dioxide) occurs as the result of combustion. Approximately 90 percent of these emissions occur as nitric oxide (NO). Thus, NO_2 is primarily a secondary pollutant arising from oxidation of NO in the atmosphere. As of 1977, there is roughly a 60-40 split in stationary-mobile source emissions of NO_x in the United States. Natural sources emit about 20 percent of the total NO_x nationwide. However, these emissions are diffuse and ambient NO_2 concentrations in remote areas are very low. Hence, natural NO_x emissions need not be included in the NO_x emission inventories used in SIP's for NO_2.

Conversion of NO to NO_2 in the atmosphere occurs via two principal mechanisms: (1) oxidation of NO by organic compounds (photochemical synthesis), and (2) oxidation of NO by ozone (titration). Titration occurs rapidly and is likely to be the primary means by which large individual sources of NO_x make their greatest impact on hourly concentrations of NO_2. A third process is the oxidation of NO by O_2 (thermal conversion); however, this process is only important in and near stacks where NO concentrations are very high. High concentrations of NO_2 found at representative monitoring sites 1/2-4 hours travel time from major source areas of NO_x and organic pollutants are likely to be largely the result of photochemical synthesis. Observed high concentrations of NO_2 are most likely to result from the impact of both synthesis and titration to varying degrees. Thus, peak NO_2 is approximately proportional to NO_x emissions unless the peak results almost solely from titration in which the conversion of NO to NO_2 is limited by the amount of available ozone. Data from continuously operated monitoring sites suggest this exception is very rare. Curves depicting diurnal patterns of NO, NO_2 and ozone observed at a monitoring site can serve as useful means for assessing whether or not an observed peak concentration of NO_2 is entirely attributable to ozone-limited titration or nearly so.

Proper design of NO_2 monitoring networks, choice of individual sites and careful data quality assurance are essential prerequisites for formulating an appropriate strategy for reducing NO_2. At a minimum, the network should incorporate (1) a station 1/2-4 hours travel time (e.g., 15 km) downwind of the most intense area of NO_x and organic emissions, and (2) a station within the most intense area of VOC and NO_x emissions. In order to obtain representative values, monitors should not be located within 200 meters of large individual sources. In screening the data for validity, it should be noted that existing data suggest that hourly NO_2 concentrations in excess of 0.40 ppm are unlikely. Values in excess of 0.40 ppm should be further scrutinized using statistical tests and, in some cases, by reviewing concurrent diurnal data for NO, NO_2, and ozone.

Long range transport of NO_2 is not a significant factor leading to peak hourly concentrations of NO_2. Comparison of urban-suburban data with rural or remote data reveal concentrations in the urban-suburban areas are very much higher. Consequently, in most cases, there is little need to consider intercity transport of NO_2 in estimating local control requirements to meet any prospective short term NAAQS for NO_2. A possible exception to this generalization is the case of several large cities, aligned by the wind, which are within several hours travel time of one another. The data base underlying this report is insufficient to examine such a case. Elevated concentrations of NO_2 sometimes observed to persist throughout the night (i.e. the "carryover" phenomenon) most likely occur as the result of poor dilution in the vicinity of sources of NO_x.

Control strategies for NO_2 need to be coordinated with strategies for reducing ozone. First, experimental evidence and modeling exercises indicate that reducing organic emissions pursuant to ozone State Implementation Plans (SIP's) may also reduce peak NO_2 concentrations attributable to photochemical synthesis. Second, reducing ozone diminishes NO_2 concentrations, formed as the result of ozone-limited titration, proportionally. Third, long range transport of NO_2, while in low concentrations, may be sufficient to aggravate violations of the ozone NAAQS in rural areas. Unfortunately, the present state of knowledge does not enable reliable quantitative estimates of this latter impact to be made.

Use of SO_2 and CO data as tracers and use of peak to mean ratios appear to be useful techniques for qualitatively assessing the impact of NO_x source categories on observed high hourly concentrations of NO_2. These techniques provide justification for assumptions incorporated in models to quantitatively estimate the impact of control programs. Tracer and peak-to-mean techniques indicate that observed concentrations of NO_2 which are greater than 0.20 ppm are almost always attributable to ubiquitous area sources, most of which are mobile sources. Hence, mobile source reductions should ordinarily be more effective on an area-wide basis than point source reductions in reducing annual average and hourly peak concentrations of NO_2. The infrequent impact of elevated point sources is attributable to the following factors: (1) during stable stratification, elevated plumes remain aloft; (2) correspondence of wind direction and distance of maximum plume impact with the location of a monitor is infrequent; (3) NO_2 monitoring networks are generally sparse. In contrast, area sources have low release heights (i.e., impact the surface during all meteorological conditions) and are distributed throughout the urban region in all directions from the monitors.

The preceding statements do not necessarily mean that an elevated point source's impact on hourly concentration is insignificant. Modeling studies have shown that areas downwind of major elevated point sources during peak NO_2 periods may experience concentrations substantially greater than the general urban levels associated with area sources, particularly if ambient levels of ozone are high. A control strategy for a given urban area should consider both the areawide NO_2 levels and "hot spots" associated with large elevated point sources. Control of both mobile and large elevated point sources may be required to meet a short-term NO_2 standard. Control of NO_x emissions from elevated point sources may also be highly desirable for other reasons (e.g., reduction in fine particulate, acid rain-forming potential and impact on downwind ozone formation).

Models to quantify the impact of control strategies can be categorized as multisource or individual source models. Several multisource models exist. These range in sophistication from photochemical air quality simulation models (AQSM's) to proportional rollback. Although they have not been extensively tested, photochemical AQSM's offer the greatest potential for evaluating prospective NO_2 control strategies. They appear to be particularly attractive alternatives in areas which have already compiled a substantial data base for the design of ozone SIP's.

Key assumptions of the proportional rollback model also appear to hold for use in evaluating broad strategies to reduce annual and hourly NO_2 concentrations. For example, both peak and mean NO_2 appear to be proportional to ambient NO_x. In addition, use of the rollback model can be supplemented with a crude assessment of the impact of reducing organic emissions described in Chapter 8. The rollback model represents an acceptable approach in an individual urban area only if some heed is given to source-receptor relationships. To reconcile findings concerning the lack of point source impact on observed high hourly and mean concentrations of NO_2 with the assumptions in rollback, the following approach is appropriate. First, unless tracer data indicate to the contrary, do not include the emissions from elevated point sources in the emission inventory used in rollback. This enables projections of future air quality to be made at existing monitoring sites which are consistent with present observations. Second, to assess the impact of major individual sources on peak hourly NO_2, superimpose predictions obtained with a point source dispersion model upon representative projected values of future NO_2 obtained with the rollback model. It may then be necessary to repeat this procedure using different (but consistent) sets of meteorological assumptions in the rollback and point source models.

There are several available models for estimating the impact of individual point sources or major roadways on NO_2. The following approach represents an acceptable compromise between sufficient detail and data availability. Utilize a Gaussian point source model to estimate maximum concentration of NO_x (i.e., $NO + NO_2$). Apply the Ozone-Limiting Approach to estimate the peak concentration of NO_2. Special cases in which a source emits NO_2 (rather than NO) directly into the atmosphere can be considered using Gaussian models and modifying the inputs of the Ozone-Limiting Approach.

1.0 INTRODUCTION

This document has two objectives. The first is to provide a concise description of the extent and likely causes of high ambient concentrations of nitrogen dioxide (NO_2). The second objective is to identify useful procedures for evaluating the effectiveness of strategies to reduce unacceptably high concentrations of NO_2. The document is intended to be of use to persons having responsibilities for:

a) determining the need for a strategy to reduce short term (e.g., hourly) and/or annual concentrations of NO_2; and

b) designing and evaluating the effectiveness of a strategy for meeting such an objective. The information presented in this document is based on reviews of general references on oxides of nitrogen (such as the Oxides of Nitrogen Criteria Document[1]), the results of laboratory and field studies conducted by the EPA and others, ambient air quality data reported to the National Aerometric Data Bank (NADB) during 1975-1977 from throughout the nation, and modeling studies.

The document is organized in the following manner. Chapter 2.0 identifies sources of emissions of NO_x. The relative importance of various major source categories is described. Since only a small fraction of the oxides of nitrogen (NO_x) emissions occur as NO_2, it is important that the means by which NO_x is converted to NO_2 be identified. Chapter 3.0 describes the most important processes by which NO_2 is formed in the atmosphere. Having described the processes by which high levels of ambient NO_2 can exist in the two preceding chapters, Chapter 4.0 describes the extent of the ambient air quality data base which has been examined, procedures for identifying data which may be spurious and existing ambient levels of NO_2.

Chapters 5-7 discuss factors which may contribute to high short term concentrations of NO_2. Chapter 5.0 examines the role of intermediate and long range transport in contributing to observed high levels of ambient NO_2. Chapter 6.0 addresses relationships between NO_2 and its two major precursors: nitric oxide (NO) and volatile organic compounds (VOC). Laboratory, modeling and empirical studies are drawn upon to surmise existing relationships between ambient NO_2 and precursors which are subject to control programs. Chapter 7.0 focuses on relationships which appear to exist between observed high levels of NO_2 and precursor emissions from several major source categories. Potential of various source categories for leading to high ambient levels of NO_2 is also discussed.

Chapter 8.0 identifies and briefly discusses modeling procedures which may prove useful in quantifying the extent of controls needed to attain air quality goals. Models which are suitable for urban wide applications, as well as those which are useful in estimating the impact of individual sources, are enumerated. The last section in each chapter summarizes the implications of material presented in that chapter on the formulation of effective strategies concerning NO_2. Hence, these last sections provide a short hand review of key implications of the present state of scientific knowledge on developing strategies for reducing ambient levels of NO_2. The remaining portions of each chapter provide a more indepth presentation of information leading to the identified implications for strategies.

2.0 EMISSIONS OF NO_x

2.1 Anthropogenic Emissions

Oxides of nitrogen (NO_x) emissions ordinarily consist of two components: nitric oxide (NO) and nitrogen dioxide (NO_2). Nitrogen dioxide is thus both a primary and secondary pollutant. A primary pollutant is one which is emitted directly to the atmosphere from a source of pollution. Some sources where most of the NO_x is emitted as NO_2 are nitric acid manufacturing plants, nitrogen fertilizer plants and munitions manufacturing. The NO_2 emissions may be up to 100 percent of the total NO_x emissions from such sources. Another source of NO_2 emissions is fuel combustion. However, only about 5-10 percent of the NO_x emissions from combustion sources occurs as NO_2. According to the National Air Quality Monitoring and Emissions Trends Report for 1977, 96 percent of anthropogenic NO_x emissions within the U.S. arise from the combustion of fuels.[1] Due to the preeminance of combustion sources, the composition of emissions from combustion sources has important implications on the assessment of ambient NO_2.

Combustion sources are comprised of two major categories: stationary fuel combustion (56 percent of the total NO_x) and combustion by mobile sources (40 percent). This leads to the conclusion that only about 10 percent of the NO_x emissions nationwide occur as NO_2. Because of the importance of combustion processes as a source of NO_x, nitrogen dioxide can be thought of chiefly as a secondary pollutant. A secondary pollutant is one which is not emitted directly by a source of pollution. Instead, secondary pollutants arise from chemical reactions in the atmosphere occurring among other primary and secondary pollutants (i.e., nitric oxide, volatile organic compounds [VOC], ozone, etc.) The chemical reactions which produce NO_2 are discussed in Section 3.0.

Since secondary NO_2 is chiefly formed through chemical reactions involving nitric oxide (NO), it is essential to investigate sources of both NO_2 and NO (i.e., sources of NO_x). For purposes of impact assessment, manmade sources of NO_x can be classified into four types:

1. stationary
2. mobile
3. point
4. area

The preceding classifications prove useful for selecting an appropriate mix of controls (mobile versus stationary) and in modeling applications (area versus point). Table 2.1 presents national NO_x emission estimates segmented into several broad source categories. Note that several of the categories identified in Table 2.1 include both point and area, as well as mobile and stationary sources. The distinctions between "area" and "point," and between "mobile" and "stationary," are as follow. Individual sources which emit large quantities of NO_x are considered explicitly in models and are hence regarded as "point" sources. Sources which, on an individual basis, emit relatively small amounts of NO_x are aggregated in models and designated as "area" sources. For example, a large isolated electrical generating power plant is considered to be a point source, whereas residential heating (due to the large number and spread out nature of housing) would be considered as an area source. The distinction between mobile and stationary is just one of ability of a source to relocate in a very short period of time. Thus, an automobile is a mobile source, whereas a power plant is a stationary source. Because the distinctions between stationary-mobile and area-point are not mutually exclusive, it is possible to categorize certain sources as "stationary-point" etc., as in Table 2.1.

Table 2.1 1977 National NO_x Emissions by Source Category (Expressed as NO_2)

Source Category	NO_x ($X10^6$ metric tons/yr)	Fraction of Total NO_x Emissions
Fuel Combustion		
Transportation (mobile-area)	9.2	0.40
Electric Utilities (stationary-point)	7.1	0.31
Industrial (stationary--point/area)	5.0	0.22
Residential-Commercial (stationary-area)	0.9	0.04
Industrial Processes		
Manufacturing (stationary-area)	0.7	0.03
Miscellaneous (area)	0.1	0
Total	23.1	1.00

2.2 Natural Sources of NO_x

Thus far, the focus has been on manmade sources of NO_x. It is appropriate to next examine whether natural sources of NO_x are likely to contribute significantly to ambient concentrations of NO_2. There is much uncertainty about the extent of natural emissions of NO_x. Estimates of global NO_x emissions from natural sources are in the order of $20\text{-}90\times10^6$ metric tons/year.[3] These estimates are arrived at indirectly by determining what they would have to be in order to balance the global NO_x cycle. Natural emissions primarily result from biological and chemical transformations in the soil and from lightning. Relatively small additional amounts (on a global basis) of NO_x arise from conversion of naturally emitted ammonia (NH_3) and from large point sources (i.e., volcanoes). Prorating natural NO_x emissions to the United States, on the basis of land area (i.e., the U.S. comprises about 6 percent of the world's land area), gives a maximum estimate of natural NO_x of about 6×10^6 metric tons/year emitted within the U.S. This latter figure is roughly 25 percent of the annual manmade emissions presented in Table 2.1. and therefore 20 percent of the total (manmade + natural) NO_x emitted nationwide.

2.3 Significance of Manmade Versus Natural Emissions

Although natural emissions constitute as much as 20 percent of the total NO_x emissions within the U.S., their impact on ambient NO_2 concentrations is likely to be much less. This assertion becomes obvious when one considers emission density rather than total emissions. It is reasonable to assume that natural emissions are distributed fairly uniformly about the country. Manmade emissions, however, are clustered near centers of habitation or in large industrial complexes. If the estimated 6×10^6 metric tons/year of natural emissions were distributed over the approximately 3,000,000 mi^2 of the contiguous 48 States, an NO_x emission density of two metric tons/year/mi^2 would result. Comparing this emission density with sample urban emission density figures presented in Table 2.2 indicates dramatic differences.[4]

The disparity between NO_x emission density attributable to natural sources and the emission density in urban areas is reflected by ambient air quality measurements. Various monitoring studies conducted in remote areas, and in rural areas of the United States, have typically reported NO_2 concentrations of less than 1 ppb to 10 ppb (i.e., .001-.01 ppm).[3,5] Maximum readings as high as 30-40 ppb have been observed in rural areas several tens of kilometers downwind from urban areas.[7] However, contributions from anthropogenic sources cannot be ruled out on these occasions. In contrast to ambient levels of NO_2 measured in rural areas, several urban or suburban monitoring sites have reported maximum hourly NO_2 concentrations in excess of 200 ppb (0.20 ppm).[8] Thus, like NO_x emission density, differences between NO_2 concentrations in urban and remote areas as great as two orders of magnitude have been observed. Prevailing concentrations of NO_2 in urban, rural and remote areas will be described in greater detail in Chapters 4 and 5.

2.4 Implications

Implications of the nature and extent of NO_x emissions are summarized below.

1. The major portion of NO_x emissions occur as NO. Hence, one needs to recognize the role of atmospheric chemistry resulting in the conversion of NO to NO_2. Selection of an appropriate NO_x control strategy will, in part, depend on being able to correctly identify factors influencing the conversion of NO to NO_2 in the atmosphere.

TABLE 2.2 NO_x Emissions in Selected Urban Counties*

Urban Area	County	Emissions tpy†	County Area mi^2	Emission Density tpy/mi^2
St. Louis	St. Louis City	46,676	61	765
	St. Louis County	80,946	499	162
Chicago	Cook	250,644	954	263
Washington, DC	Washington	40,794	61	669
Minneapolis	Hennepin	54,243	567	96
Richmond	Henrico	12,980	232	56
Houston	Harris	214,419	1,723	124

* NEDS data base
Area emissions as of June 6, 1979
Point emissions as of October 2, 1979

† tpy = tons per year

2. Although most (90 percent) manmade NO_x emissions occur as NO, there are some manufacturing processes which result in significant amounts of NO_2 being directly emitted as a primary pollutant. Such emissions have the potential for causing locally severe short-term peaks of NO_2.

3. On a national basis, 1977 emission estimates indicate approximately 60 percent of anthopogenic NO_x emissions result from stationary sources, with the remaining 40 percent arising from mobile sources. This suggests that potential for reducing ambient levels of NO_2 is available through emission reductions from stationary or mobile sources, or both.

4. Although natural NO_x emissions are about 25 percent of the manmade emissions within the U.S., the emission density (i.e., emissions/area) of natural emissions is very much less than that for manmade emissions in urban areas. Ambient measurements of NO_2 in urban and remote areas indicate urban concentrations of NO_2 are as much as two orders of magnitude greater than concentrations in remote areas. This information indicates that natural emissions of NO_x would contribute an insignificant amount to any conceivable NAAQS for NO_2. Therefore, natural emissions of NO_x can be ignored in the formulation of strategies for reducing unacceptably high levels of NO_2.

3.0 MECHANISMS FOR NO_2 FORMATION IN THE ATMOSPHERE

Observed concentrations of NO_2 are chiefly the result of chemical reactions in the ambient air involving NO and other pollutants. In order to reduce NO_2 levels, it is important to know how the NO_2 is formed in the atmosphere. Since there are several potential pathways responsible for this formation, proper identification of the significant path leading to particular violations of NAAQS for NO_2 is vital in selecting appropriate controls and in properly designing SIP's.

In subsequent sections, different mechanisms or formation processes will be discussed. Each process will be outlined and its implications about the effectiveness of various control strategies described. In the later sections, it will become apparent that the mechanisms presented either involve ozone directly or precursors of ozone. This indicates that close coordination is needed between NO_2 control programs and ozone control programs.

The three major phenomena with potential for leading to high NO_2 are:

1. photochemical synthesis;
2. the reaction of nitric oxide with ozone (titration);
3. carryover.

Each process will now be discussed. Typical diurnal patterns of ambient NO_2 concentration are presented, illustrating each of the above phenomena. Next, findings are discussed which concern: (1) observed frequency with which each phenomenon corresponds with high concentrations of NO_2, and (2) the correspondence (or lack thereof) between the occurrence of high NO_2 concentrations and physical location of a site. As described in Chapter 4.0, the quantity of available NO/NO_2 data is much greater in California than in the rest of the nation.

For this reason a distinction is made in the subsequent discussion between analyses conducted with California data and with other data.

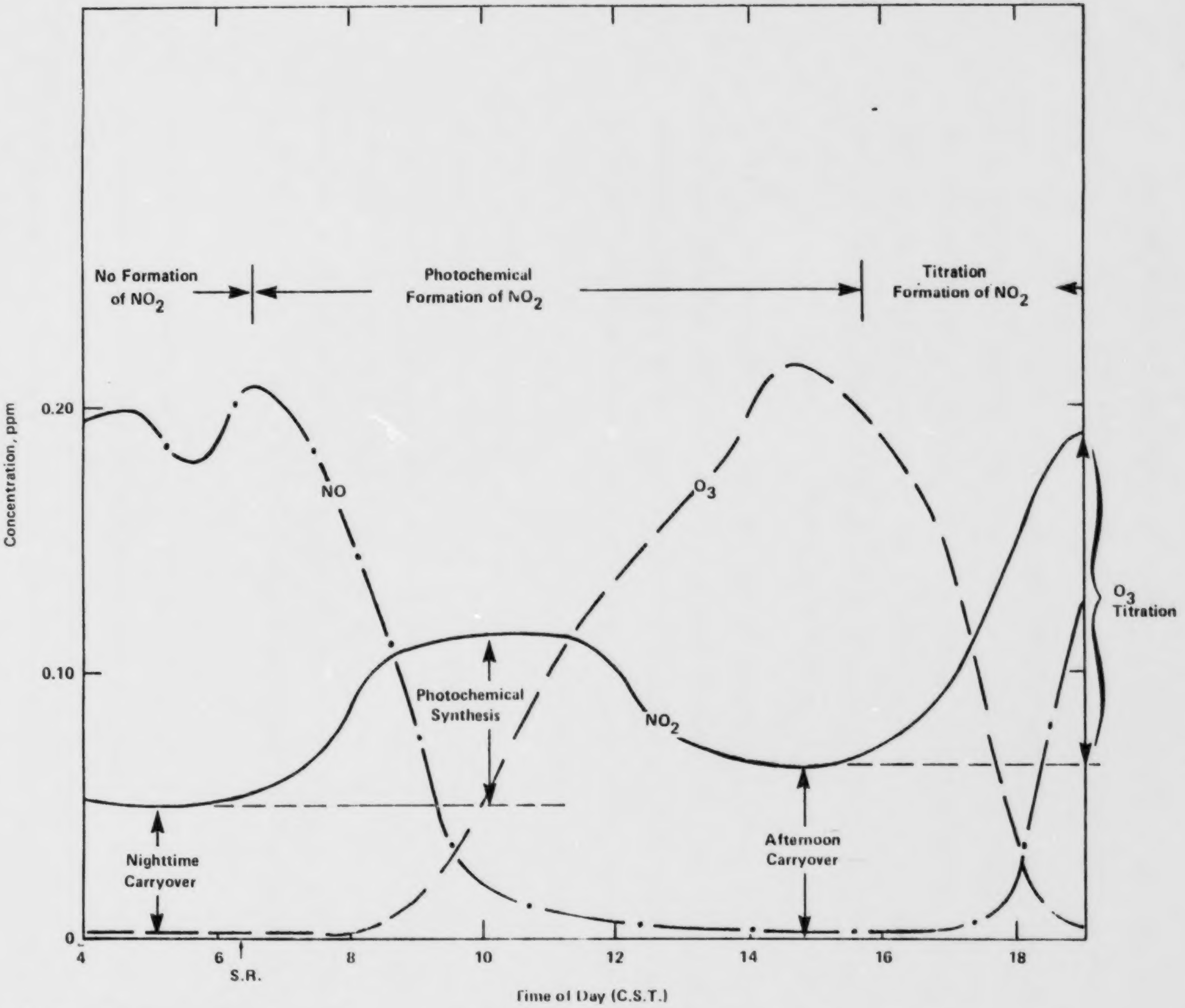
3.1 Photochemical Synthesis of Nitrogen Dioxide

Photochemical synthesis occurs when chemical reactions are initiated by radiant energy (sunlight). More specifically, mixing of nitric oxide (NO) and non-methane organic compounds (NMOC) in the presence of sunlight leads to chemical reactions which produce NO_2. This process usually results in maximum NO_2 concentrations occurring a few hours after sunrise.

Photochemical synthesis of NO_2 may occur at any time during the daytime hours; however, the speed with which the NO_2 is formed and destroyed is a function of sunlight intensity and precursor concentrations. Thus, the large concentrations of NO and NMOC in the mid morning (sunrise-1100 LDT) will more readily produce larger amounts of NO_2.

Photochemical synthesis of NO_2 occurs throughtout the year. Monitoring data described in Chapter 4.0 suggest that the severity of wintertime and summertime NO_2 peaks are comparable. One difference between seasonal NO_2 peaks attributable to synthesis is that during winter peak NO_2 concentrations may occur later in the day. This is due to the reduced sunlight intensity during the winter months and the resulting slower production of organic radicals causing conversion of NO to NO_2.

Figure 3.1 provides an illustration of summertime photochemical synthesis. The data shown in Figure 3.1 were observed by averaging pollutant concentrations at four sites in the St. Louis RAPS on October 1, 1976. Typically, photochemical synthesis begins shortly after sunrise. The morning traffic peak combines with


No Formation of NO_2
Photochemical Formation of NO_2
Titration Formation of NO_2
0.20
0.10
0
Concentration, ppm
NO
O_3
NO_2
Photochemical Synthesis
Nighttime Carryover
Afternoon Carryover
O_3 Titration
4
6
8
10
12
14
16
18
S.R.
Time of Day (C.S.T.)

adverse meteorological conditions to produce the high concentrations of precursors (NMOC and NO) needed to sustain the production of high concentrations of NO_2. Later, emissions are substantially reduced and/or meteorological conditions improve (note the diurnal carbon monoxide pattern roughly corresponds to the decrease in NO_x concentrations).

A review of diurnal patterns of NO_2 and ozone using 1975-77 data for California indicates that photochemical synthesis accounts for 56 percent of the 5400 site hours with NO_2 concentrations reported in excess of 0.20 ppm.[9] A similar review of data was undertaken for the rest of the United States.[10] The results indicate that about 32 percent of the occasions where NO_2 exceeded 0.20 ppm can be unambiguously attributed to photochemical synthesis.

The physical location of a site which primarly experiences high NO_2 concentrations, due to photochemical synthesis, is one within several (e.g., 1-4 hours) hours travel time of where heavy NO_x and VOC emissions occur. These areas are usually located in urbanized or larger industrialized areas where primary emissions of NO_x and VOC are both plentiful.

3.2 Titration

Titration is defined as the reaction between ozone and nitric oxide.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3.1)$$

This reaction can occur at any time of the day, since it is not dependent on the presence of sunlight. In reviewing diurnal patterns of NO_2 and associated pollutants, however, the most marked impact of titration in contributing to high levels of NO_2 occurs in the late afternoon or early evening. Ozone formed in the late morning or early afternoon, mixes with the fresh afternoon NO_x emissions to form NO_2. This reaction occurs very rapidly in the atmosphere, unlike the photochemically driven synthesis which proceeds more slowly.

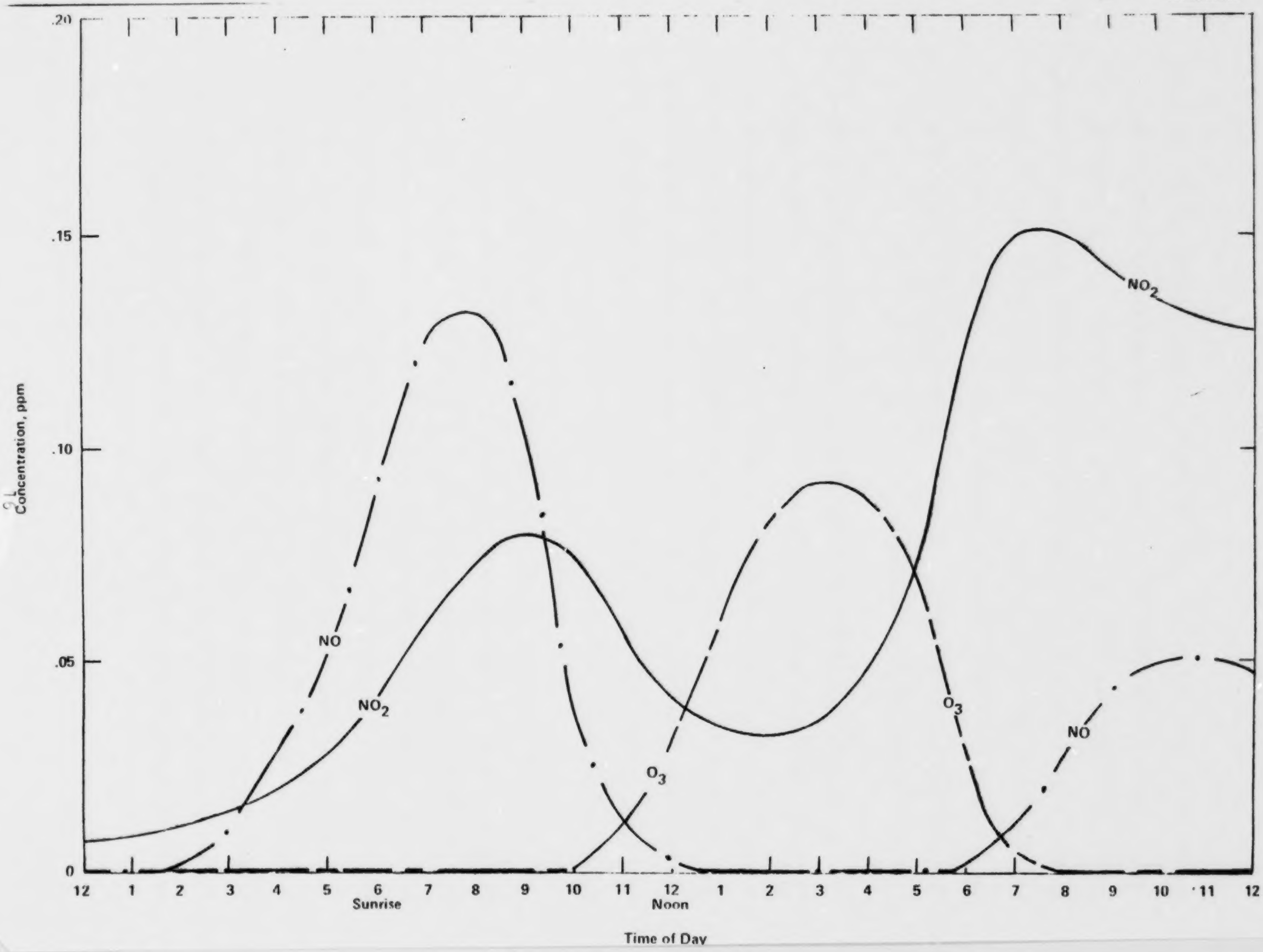
The speed of the titration reaction is clearly illustrated by ambient measurements collected near a section of the San Diego Freeway in Los Angeles.[11] In this study, NO_x monitors were deployed upwind and at varing intervals downwind from the roadway. Indications are that the NO in the roadway plume is converted by the O_3 in dilution air. This was observed within 10's of feet from the roadway, indicating a conversion time of a few minutes or less.

A sample diurnal concentration profile illustrating titration is presented in the right-hand portion of Figure 3.1 (page 12). Note that the amount of NO_2 produced after 1500 is not greatly different than the amount of ozone present at 1400 hours. As Equation 3.1 states, one part NO plus one part O_3 yields one part NO_2. However, when analyzing ambient data, other processes are taking place simultaneously. For example, direct emissions of NO_2, some photochemical production of NO_2 still occurring, and a smoothing effect of a one-hour averaging time may lead to varied amounts of NO_2 being observed while O_3 is declining. Consequently, even when titration is the predominant means by which NO_2 is formed, an observed increase in NO_2 may not coincide precisely with an observed decrease in O_3.

The amount of NO_2 formed through the titration reaction is limited either by the available NO or by the available O_3. It is important to be able to identify which of these two factors limits the NO_2, because of the underlying implications on what would constitute an effective control strategy. Clues as to which factor is limiting may be obtained by examining diurnal concentration profiles of NO_2, NO and O_3. Such an examination leads to one of two possible outcomes: (1) the amount of NO_2 produced is less than the amount of ozone observed, or (2) the ozone is depleted and excess NO is present. Either case has the potential to produce more NO_2. The first case is termed "NO limiting." This is where NO_x emissions (primarily NO) are not sufficient to mix with the ozone present, thereby limiting the amount of NO_2 produced. The second case is called "ozone limiting," and occurs if insufficient ozone is present to convert available NO to NO_2. Figures 3.2 and 3.3 are hypothetical diurnal patterns of O_3 limiting and NO limiting cases of titration respectively.

In the case where titration formation of NO_2 is limited by available ozone, O_3 control programs should be effective in reducing peak NO_2. In such a case, a reduction in ambient ozone levels should result in a corresponding reduction in NO_2. On the other hand, if the amount of NO_2 formed is limited by the availability of NO_x, programs to reduce ozone will affect ambient NO_2 resulting from titration to a lesser extent until the O_3 is reduced to a level where its availability limits the amount of NO converted to NO_2.

Data bases in California and in the remainder of the nation have been reviewed to ascertain the frequency with which titration reactions appear to be the predominant cause of peak observed NO_2. In California, diurnal NO, NO_2 and ozone concentration patterns suggest that titration was primarily responsible for 40 percent of the hourly NO_2 values in excess of 0.20 ppm. The more limited data base in the remainder of the nation however indicates that in only about 8 percent of the instances in which NO_2 is in excess of 0.20 ppm does afternoon titration appear to be a principal contribution to the high observed NO_2. An indication as to what type of site might experience afternoon reaction of O_3 and NO is also available from the California data analysis. In the Los Angeles Air


.20
.15
.10
.05
0
Concentration, ppm
NO
NO$_2$
O$_3$
NO$_2$
O$_3$
NO
12
1
2
3
4
5
6
Sunrise
7
8
9
10
11
12
Noon
1
2
3
4
5
6
7
8
9
10
11
12
Time of Day

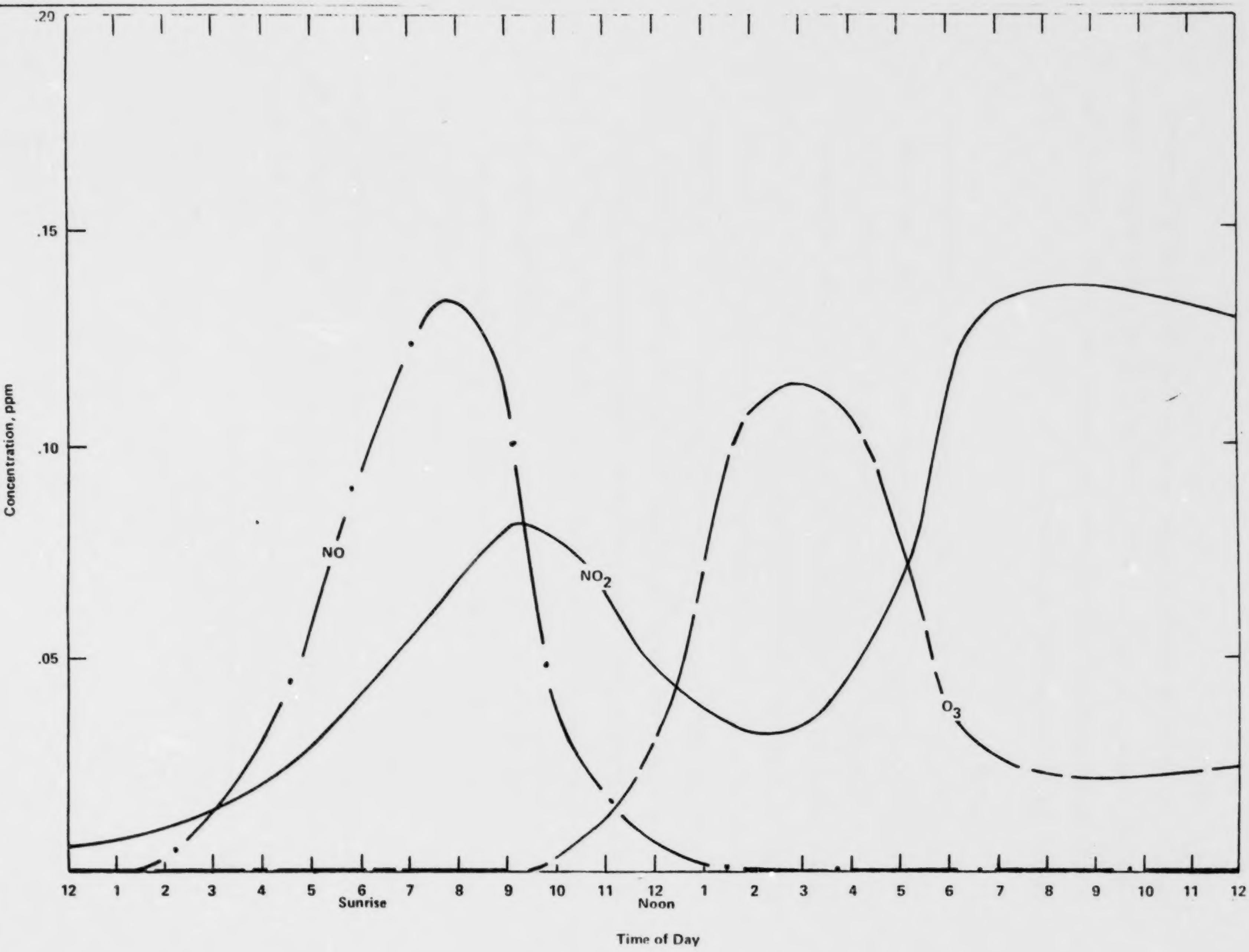


Figure 3.3 NO Limiting Case of Titration

Basin, sites which are usually impacted by transported O_3 frequently experience peak late afternoon NO_2 peaks in which titration is an important factor. Presence of transported ozone alone is not sufficient however. It is also necessary that the monitor be located near large sources of NO_x.

3.3 Carryover

Carryover is a condition in which relatively high NO_2 concentrations persist for several hours (e.g., overnight). Carryover can occur at any time of day. If it persists throughout the night, it is termed "nighttime" carryover. If it occurs during the late morning to early afternoon, it is termed "afternoon" carryover. Carryover, whenever it occurs, is not a formation process. Rather, it serves as a base upon which other mechanisms add additional NO_2. Examples of afternoon and nighttime carryover are illustrated in Figure 3.4. Note that in the example shown the carryover in the afternoon is carryover upon which O_3-limited titration builds. The carryover which occurs in the early morning is nighttime carryover upon which photochemically produced NO_2 subsequently builds.

Presence of carryover NO_2 as a base upon which NO_2 peaks formed by synthesis or titration can build has important implications concerning effectiveness of reducing NO_x emissions. It means that it is most likely that an NO_2 peak is the result of both synthesis and titration. Thus, even when diurnal concentration patterns suggest that a peak is primarily the result of ozone-limiting titration, reduction of NO_x emissions should reduce observed peak NO_2. The reduction in NO_2 would occur as a result of the reduction of the base (i.e., carryover NO_2) upon which the ozone-limiting titration peak builds.

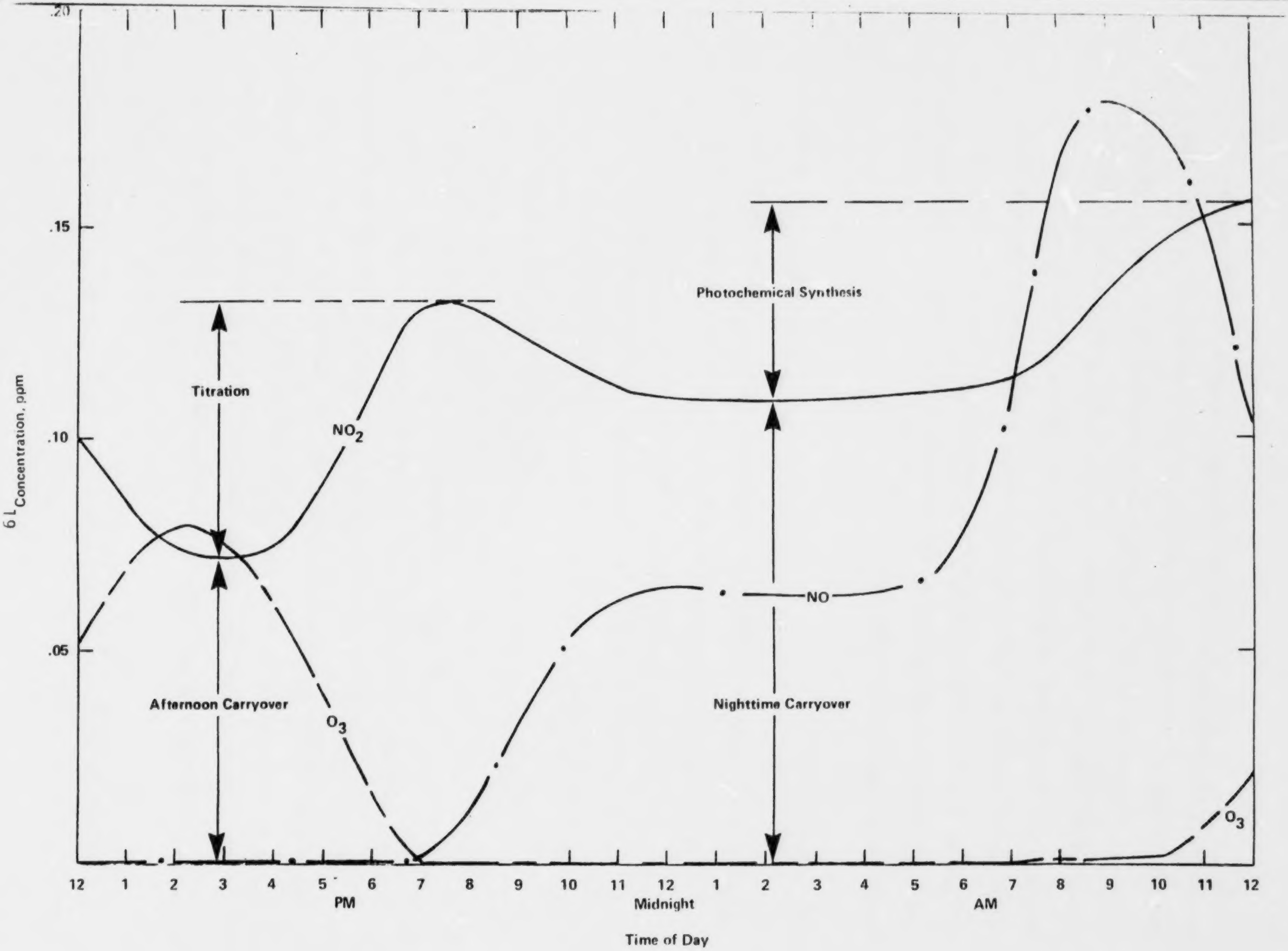


Figure 3.4 Diurnal Concentration Profiles Illustrating Carryover.

There is no single explanation for carryover. In some cases it may result from NO_2 emitted or produced upwind and transported to the monitoring site. Use of the term "transport" in this context implies a movement of an urban plume of NO_2 less than a few tens of kilometers. In other cases, carryover NO_2 is locally generated and then trapped in a stagnant or very slow moving air mass. A sea breeze may also cause a recycling of an air mass, thereby causing the persistance of high NO_2 concentrations. The underlying meteorological basis for carryover is that poor dispersion will not allow rapid dilution of NO_2 to occur. This results in NO_2 remaining high for several hours.

3.4 Implications

1. Since NO_2 is primarily a secondary pollutant, understanding the means by which it is formed is important in formulating effective control strategies. Two formation mechanisms have been identified: photochemical synthesis and the titration reaction with ambient ozone. A third phenomenon, "carryover," results from the persistence of high NO_2 over several hours. However, NO_2 which is "carried over" originates from either synthesis, titration or both.

2. If synthesis is identified as the major cause of observed violations, control of NO_x emissions should be effective in reducing ambient NO_2. This subject will be discussed further in Chapter 6.0. If titration is the prime cause for high NO_2, efforts need to be made to determine whether NO_x or ozone is the limiting factor. If the limiting factor is NO_x, reduction of NO_x emissions should prove effective in reducing ambient NO_2. If ambient NO_2 is limited by the amount of available ozone, reducing NO_x emissions should nevertheless be effective, because the carryover NO_2 upon which a peak attributable to ozone-limited titration builds, should be reduced. Only in a rare case where diurnal curves suggest

ozone limited titration will little or no carryover would control of NO_x emissions be relatively ineffective. Even in this unusual case, some reduction of NO_2 would result from NO_x controls by virtue of some of the NO_x being emitted as NO_2 as a result of instack oxidation reactions.

3. Reviewing the diurnal sequence of NO_2, NO and O_3 concentrations is a useful approach for estimating whether an observed NO_2 peak concentration is associated with synthesis or titration. Such information can be effectively displayed using the graphical procedures illustrated in this chapter. These graphs may also be useful in detecting the presence of carryover assessing whether NO_2 peaks are formed primarily as the result of titration is limited by available NO_x or by available ozone.

4. Although the graphical techniques described herein are useful in identifying NO_2 formation processes, frequently the information they yield may be ambiguous. Information on monitor siting, together with the knowledge that the titration reaction is faster than photochemical synthesis of NO_2, may help resolve some ambiquities arising from diurnal concentration profiles. If a monitor is in close proximity to a major source of NO_x (e.g., within a few hundred meters of a major highway or in position to be directly impacted by a point source plume), titration may be the predominant explanation of high observed NO_2. If a monitor is located downwind (e.g., 1/2-4 hours travel time) from major sources of NO_x and volatile organic compounds (VOC), photochemical synthesis may be important in leading to high concentrations of NO_2.

4.0 MONITORING, DATA QUALITY AND THE OBSERVED EXTENT OF HIGH NO_2 CONCENTRATIONS

In Chapters 2.0 and 3.0, NO_x emissions and processes by which these emissions may lead to high concentrations of NO_2 were discussed. This information serves as important input in the design of appropriate control strategies. There is an even more fundamental question, however. How does one know whether controls are required in the first place? The need for control programs for NO_2 is largely determined by reviewing ambient air quality data. Not only that, but the extent of required emission controls may depend on these data as well. Consequently, the importance of obtaining high quality data which are representative of what one is trying to measure cannot be overemphasized. Issues pertaining to data quality can be subdivided as follows: (1) use of appropriate instrumentation, siting criteria and operating procedures, and (2) review of recorded data to check for spurious values.

4.1 Network Design and Operation

Regulations and guidance concerning appropriate instrumentation and operating principles is provided elsewhere.[12,13] State and Local Air Monitoring Stations (SLAMS) exist to meet the data needs of individual State/local agencies. As such, it is the SLAMS network which must be responsive to the needs for identifying the extent to which a particular city is out of compliance with existing NAAQS and the extent to which particular sources of NO_x may deteriorate ambient air quality.

Information and references cited in Chapter 3.0 can be useful in designing a SLAMS network which is likely to detect high NO_2 concentrations. Recall from Section 3.1 that a review of California data suggests that highest NO_2 concentrations attributable to synthesis occur within or immediately downwind of areas with greatest NO_x and VOC emissions. Interpretation of diurnal NO_2 patterns typifying synthesis suggests that the maximum impact on ambient NO_2 occurs in the mid-morning to early afternoon within about 1-4 hours travel time of maximum emissions. Thus, the location of maximum NO_2 attributable to synthesis depends on the prevailing winds. In order to cover both the case of atmospheric stagnation and the case of light, but identifiable, resultant winds, it is recommended that stations be established within the downtown area and within 15 km of the downtown area in directions of commonly occurring winds.

Because of the need to obtain representative data in making attainment/nonattainment decisions and in designing control strategies, existing siting criteria should be adhered to. The salient features of this guidance are:

1) Inlet probe height located 3-15 meters above ground and at least one meter away from supporting structures.

2) There must be unrestricted air flow in at least three of the four cardinal wind directions. It is not desirable to locate an instrument within 20 meters of trees nor is it appropriate to position an inlet probe along a vertical wall.

3) Monitors should not be located within 20 meters of any road nor within 250 meters of any road with average daily traffic (ADT) in excess of 10,000 vehicles per day. For roads with ADT of 1000-10,000 vehicles/day, the monitor should be located no closer than 20-250 meters away. The exact limitation in this latter case is determined by linear interpolation based on traffic flow. For example, if the ADT of a nearby road is 5000 vehicle/day, the monitoring probe should not be within 103 meters of the road.

If the purpose of a monitoring station is to document the impact of a particular source of emissions, siting specifications for the station may be somewhat different. If a source is a primary source of NO_2 and its emissions occur near ground level, station location should be as near to the source as one could reasonably expect the public to be for a period consistent with that specified in a NAAQS. The issue of what is a "reasonable" monitoring location for such purposes is not a technical issue, but a political and philosophical one. As such, it is outside the scope of this document. If a source's NO_x emissions occur primarily as NO, its maximum impact will most likely arise as a result of titration with ambient ozone. As discussed in Section 3.2, titration of an NO_x plume occurs very rapidly upon mixing with dilution air. Hence, siting guidance should be consistant with that for a primary source of NO_2 described above.

The problem of monitor siting for estimating the impact of a large, elevated point source of NO_x is difficult to resolve. Complications are introduced as a result of several factors:

1) the probability of observing the impact of a source at any particular monitoring station at a given time is small;

2) there is a tradeoff which occurs between dilution and chemistry within a plume. If the plume does not undergo substantial dilution, conversion of NO to NO_2 via the titration reaction may be suppressed. Conversely, if ample dilution occurs, significant conversion of NO to NO_2 may occur, but it may be difficult to distinguish between the impact of the plume and that of background air.

The implications introduced by the two preceding observations will be discussed at greater length in Chapters 7.0 and 8.0. Maximum impact from an elevated plume results from a complex combination of meteorology, source operating characteristics and terrain. Deployment of a monitoring network to estimate maximum impact from an elevated source of NO_x is best done on a case-by-case basis. However, generally appropriate monitoring guidance is to orient stations along the wind axis associated with highest ozone concentrations, paying particular attention to intermediate distances (e.g., 2-8 km for power plants). At those intermediate distances, dispersion is sufficient to bring an elevated plume to the earth's surface and to mix the plume's NO with ambient ozone. At greater distances, dilution may be expected to diminish concentrations. Even if these procedures are followed, a network may sometimes have difficulties detecting the peak impact of a source. Thus, modeling the impact of an elevated point source on ambient NO_2 may sometimes provide a better indication of such a source's maximum impact than data from available monitoring networks.

4.2 Data Quality Assurance Techniques

Even assuming monitoring instruments are properly deployed and operated, there is a need to screen the resulting data for spurious values. As many as three types of screening procedures could occur. First, observed concentrations of NO_2 should be compared with existing screened data from other sites. If values higher than NO_2 peaks typically reported elsewhere are observed, grounds for closer scrutiny exist. A second screening test which should be routinely applied is the use of computerized statistical procedures to identify peculiar gaps or patterns (e.g., spikes) in the data. These procedures are easy to apply and have been described at length elsewhere.[14] In the event the first two stages fail to resolve whether a questionable data point is or is not valid, procedures described by Richter et. al[15] can be used to provide a more rigorous test. These latter procedures require one to plot diurnal patterns of NO_2, NO, ozone and, if available, carbon monoxide (CO), and sulfur dioxide (SO_2) concentrations observed at a site. Examination of three consecutive days (i.e., bracketing the day recording the suspicious data) should allow the observer to identify errors which otherwise would be difficult to detect. Examples of such errors might include miscoding of NO_2 as NO_x or apparent drifts in the baseline data recorded by an instrument. The exact procedures are described in detail elsewhere.[15]

4.3 NO_2 Concentrations Observed in Excess of 0.20 ppm

The first data quality check recommended in Section 4.2 is to note whether a high recorded data point is consistent with previously observed data. To facilitate such a comparison, this section summarizes findings of a review of ambient hourly NO_2 concentrations of 0.20 ppm or greater which were observed from 1975-1977 inclusive. During these three years, the vast majority of hourly NO_2 observations were made within the State of California.

During 1975-77, 161 hourly NO_2 concentrations of 0.20 ppm or more were observed from approximately 40 different sites outside of California. All such values were less than 0.50 ppm, with values in excess of 0.40 ppm being extremely rare. Figure 4.1 illustrates that, although high NO_2 concentrations appear to occur more frequently in summertime, a significant number occur during the other seasons as well.

At any given location, diurnal patterns of NO_2 reflect monitor location, as well as meteorology and source configuration. Figure 4.2 represents a composite

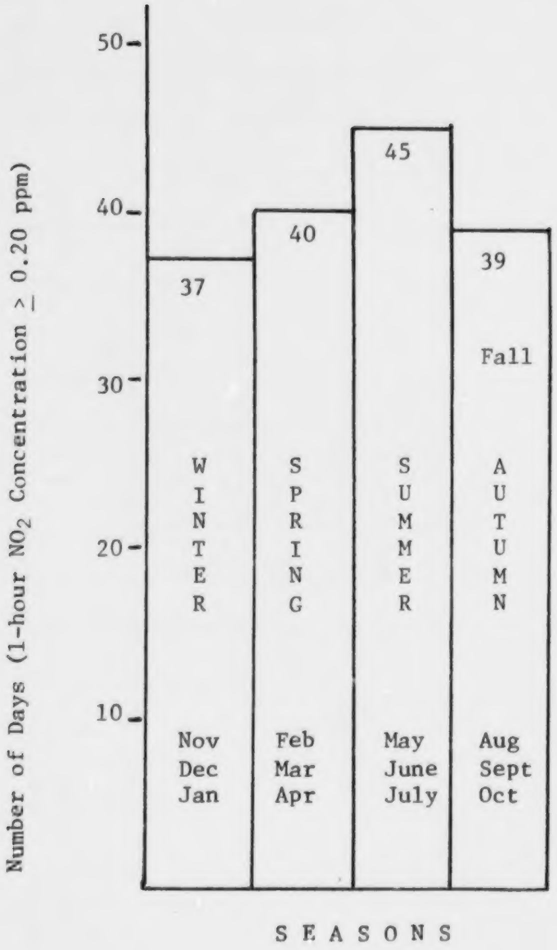


Figure 4.1 Seasonal variation in hourly NO_2 levels exceeding 0.20 ppm at all non-California stations reporting to SAROAD during 1975-77.

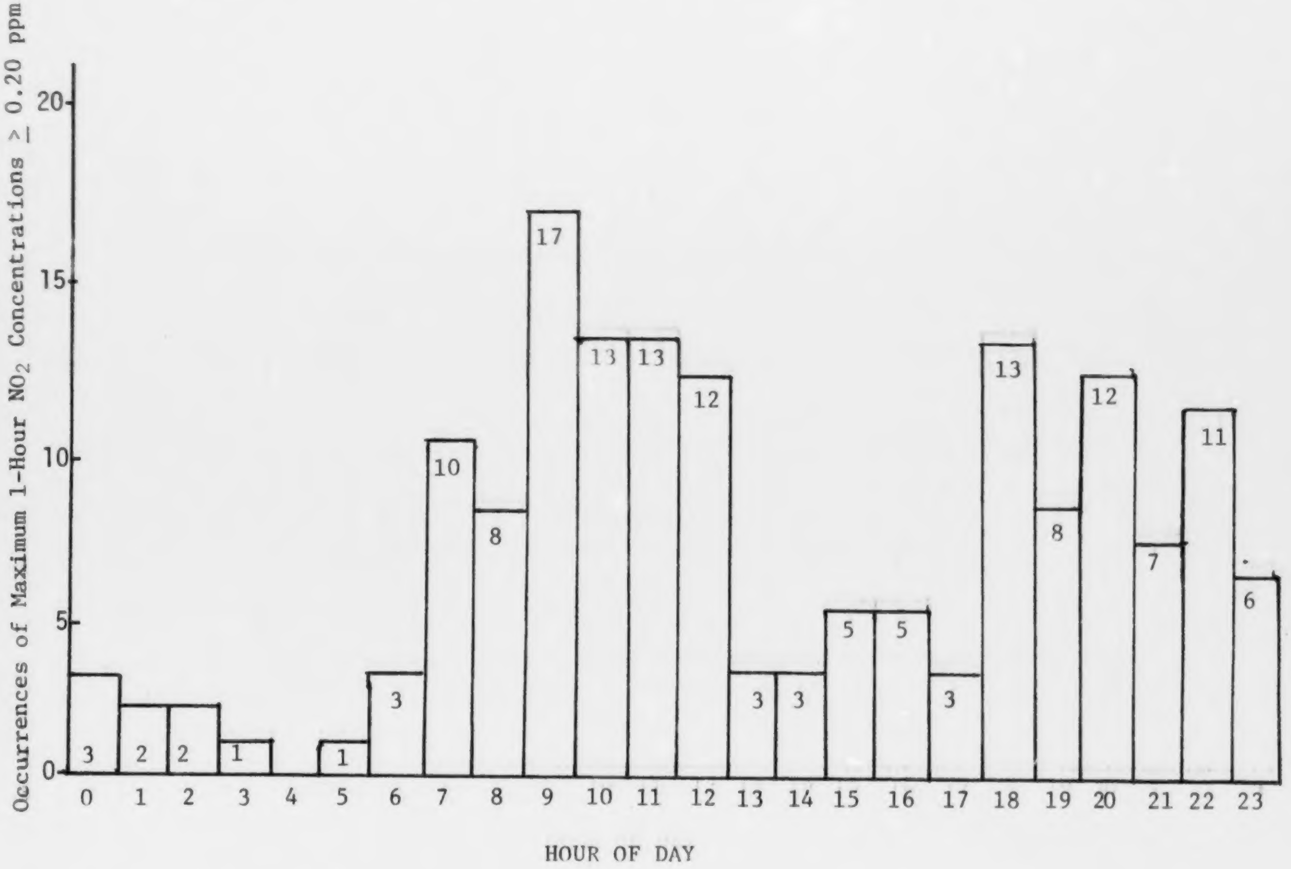


Figure 4.2 Frequency of maximum 1-hour NO_2 concentrations $\geq$ 0.20 ppm.

of all monitor stations, outside of California, in which frequency of observing high NO_2 is plotted against time of day. It is clear that high NO_2 has been observed at all times. However, the distribution in Figure 4.2 has a distinct bimodal pattern, with a primary peak between 0700-1200 and a secondary peak between 1800-2300.

In contrast to the NO_2 data base outside of California, the data from that State are extensive. Further, screening procedures similar to those described in Section 4.2 suggest that the data are of high quality.[9] The California data base examined for 1975-77 consists of data from 54 stations. Approximately 50 of these stations were found to have at least one valid observation of hourly NO_2 concentrations $\geq$ 0.20 ppm. Approximately half (26) of the stations are located in the Los Angeles area (Los Angeles, Orange, Riverside and San Bernardino Counties), with nine stations in the San Francisco Bay and six stations in the San Diego areas. However, more than 90 percent of the NO_2 values 0.20 ppm or greater occur in the Los Angeles area. Hence, the California data which are of greatest interest are heavily weighted by observations in the Los Angeles area.

Table 4.1 presents the distribution of NO_2 values $\geq$ 0.20 ppm observed in California during 1975-77. The values in Table 4.1 have been adjusted downward by 13 percent to account for a 10-17 percent reduction which needs to be made to the raw data.[9] The adjustment is necessitated as a result of revisions needed in the calibration procedure employed during 1975-77 in California. Hence, the data in Table 4.1 should be viewed as only approximately correct. Nevertheless, they are adequate to provide a basis for screening questionable data, as described in Section 4.2. Highlighting some of the information in Table 4.1, one sees that a full 50 percent of the values reported to be 0.20 ppm or greater are 0.23 ppm or

Table 4.1. Distribution of NO_2 Concentration $\geq$ 0.20 ppm for all California Monitoring Stations, 1975-1977*

Concentration (ppm)†	Number of Hours‡	Cumulative Percentage of rdgs > .20 ppm	Approximate Cumulative Percentage of all hours[1]	Concentration (ppm)†	Number of Hours‡	Cumulative Percentage of rdgs > .20 ppm	Approximate Cumulative Percentage All Hours
.20	631	17.6	99.72	.37	31	98.2	>99.99
.21	604	34.5		.38	9	98.5	
.22	448	47.0		.39	11	98.8	
.23	628	64.6		.40	10	99.08	
.24	252	71.6		.41	6	99.25	
.25	156	76.0	99.92	.42	7	99.44	
.26	169	80.7		.43	2	99.50	
.27	92	83.3		.44	5	99.64	
.28	104	86.2		.45	2	99.69	
.29	81	88.4	99.96	.46	2	99.75	
.30	119	91.8		.47	2	99.80	
.31	53	93.2		.48	1	99.83	
.32	40	94.4		.49	2	99.89	
.33	36	95.4		.50	1	99.92	
.34	32	96.3		.51	0	99.92	
.35	25	97.0	99.99	.52	2	99.97	
.36	15	97.4		.53	0	99.97	
				.54	1	100.00	

* Where simultaneous chemiluminescent and colorimetric measurements were made, only colorimetric data have been used in this table.

† Median of all concentrations $\geq$ 0.20 = 0.23 ppm

‡ Total hours > 0.20 ppm = 3579

[1] All hours estimated by multiplying (54 stations)(3 years)(365 d/yr)(24 hr/d)(.75 assumed fraction of reported values $\approx$ 1,060,000.

less. Second, only about 0.3 percent of the estimated total number of hourly NO_2 concentrations reported are 0.20 ppm or greater. Directing attention to the upper end of the scale, less than 1 percent of the values reported as 0.20 ppm or greater were ≥ 0.40 ppm. These high values constitute less than 0.01 percent of the estimated total number of observations. Out of a sample of approximately one million site-hours, there are only four hourly values reported as high as 0.50 ppm or greater.

Hence, both the California and non-California data suggest that hourly NO_2 concentrations of 0.40 ppm or more are likely to be extremely rare. There are other similarities between the data bases as well. In California, as elsewhere, NO_2 concentrations of 0.20 ppm or more occur throughout the year. However, in California, values in excess of 0.20 ppm appear to occur most frequently during the winter months. Similarly, high NO_2 concentrations can occur during any hour of the day, but are most pronounced during 0600-1300 and 1400-2100 local time.

4.4 Implications

1. Proper design of a NO_2 monitoring network, use of reference or equivalent measurement methods, and adherence to careful quality assurance procedures are essential prerequisites to the design of appropriate control strategies. Published guidance should be followed on the use of appropriate instrumentation and quality assurance procedures.[13] Network design needs to recognize the rapidity with which NO_2 is formed, source configuration and prevailing meteorology. Monitoring stations in the following locations are suggested.

a) Stations should be located one-half to four hours travel time downwind from the most intense area of VOC and NO_x emissions (e.g., 15 km) in commonly prevailing daytime wind directions with light winds.

b) At least one station should be located within the area of most intense NO_x and VOC emissions to account for stagnation conditions, possible carryover and high NO_2 due to titration. However, such station(s) should be located at least 200 meters from major sources so that the station(s) is not unduly impacted by nearby individual sources.

c) Efforts to assess the impact on NO_2 of a single source of NO using monitoring data will most likely require a special purpose monitoring network. Such a network is best designed on the basis of case-by-case modeling studies. However, it is generally most appropriate to orient stations along the wind axis most closely associated with highest ozone concentrations. Maximum concentrations may generally be expected to occur at intermediate distances downwind (e.g., 2-8 km).

2. A second essential prerequisite to designing an appropriate SIP control strategies is to screen ambient data for erroneous values. Three screening procedures have been identified:

a) Compare values with high NO_2 concentrations observed in the city or in other similar cities elsewhere. If a value is outside the range of existing observations, it should be subject to further scrutiny.

b) Employ routine computerized tests which have been designed to flag questionable values.

c) Plot diurnal concentration patterns for NO_2, NO, O_3 and, if possible, CO and SO_2. Curves should be plotted for 72 hour periods, centered on the day with questionable NO_2 readings. The diurnal curves can then be used to identify inconsistencies among pollutants.

Because they are easy to apply, it is recommended that the first two procedures be applied on a routine basis. The third procedure should be used to help resolve uncertainties about individual data points which are raised by either of the first two tests.

3. A review of ambient NO_2 data from 1975-1977 inclusive suggests the following:

a) Ambient NO_2 concentrations as great as 0.40 ppm are extremely rare indeed. Values in excess of 0.40 ppm should be given close scrutiny prior to basing a control strategy upon them.

b) Hourly NO_2 concentrations in excess of 0.20 ppm may occur during any time of the year. Hence, it is not appropriate to confine monitoring efforts to certain seasons of the year.

5.0 TRANSPORT OF NO_2

In discussing "transport" of a pollutant, it is important to identify the geographic scale of the transport. Transport of high concentrations of NO_2, unlike ozone, appears to be limited to perhaps 100-200 km, even under adverse meteorological conditions. In support of this contention, Section 5.1 describes NO_2 gradients observed in the vicinity of urban areas. Section 5.2 then summarizes recent observations made in rural areas. Section 5.3 summarizes available information on the chemical stability of NO_x (i.e., NO + NO_2) in the atmosphere and the nature of the reaction products. This latter information helps provide insight into possible upper limits to the transport of high NO_x concentrations and into relationships with long range transport of ozone. Finally, Section 5.4 identifies the implications of the foregoing information on the design of appropriate control strategies to reduce unacceptably high levels of NO_2 and ozone.

5.1 Urban Gradients of NO_2

The two urban areas with the most extensive available NO_2 monitoring data within the U.S. are Los Angeles and St. Louis (as a result of the RAPS data base). These two cities represent distinctly different examples for characterizing urban NO_2 gradients. In the former case, the city is surrounded by many miles of urban development. Further, the area is frequently characterized by unfavorable meteorology (i.e., light winds and the presence of a subsidence inversion restricting the extent of vertical mixing). Finally, the terrain in the Los Angeles Basin frequently serves to channel the flow of pollutants to downwind areas. These conditions combine to maximize NO_2 levels, as well as the area over which high NO_2 can occur.

In contrast, St. Louis is surrounded by less extensive suburbs. Prevailing meteorology is more favorable to the rapid dilution of pollutants, and there is little channelization of windflow. Hence, a review of St. Louis data should provide insight into the extent of transport from an urban area under more favorable (and, perhaps, more typical) conditions.

Table 5.1 presents maximum hourly NO_2 concentrations and the frequency with which high (> 0.20 ppm) NO_2 concentrations occurred at 23 monitoring sites in the vicinity of Los Angeles during 1975-77. Figure 5.1 has grouped the data in Table 5.1 into the following categories: observations made within 10 miles of downtown Los Angeles; observations made 10-20 miles away; 30-50 miles away; 50-70 miles away. It is clear that, despite the fact that NO_2 is a secondary pollutant, the NO_2 problem is likely to be most severe in the vicinity of source-intensive areas. For example, in Figure 5.1, the average number of hourly NO_2 concentrations in excess of 0.20 ppm diminishes from 439 at sites within 10 miles of downtown Los Angeles to 17 at sites 50-70 miles from Los Angeles. Similar reductions in maximum hourly NO_2 concentrations are experienced as well. In Figure 5.1, for example, the typical maximum hourly NO_2 concentration of 0.50 ppm observed within 10 miles of downtown Los Angeles is reduced to 0.27 ppm at sites 50-70 miles away.

It should be remembered that the Los Angeles area is one of sprawling urban development. Hence, the frequency and magnitude of recorded high hourly concentrations of NO_2 are not entirely attributable to transport from the most source-intensive area (50-70 miles upwind). Methods similar to those described in Chapter 3.0 can sometimes be used to distinguish whether observed high hourly concentrations of NO_2 are attributable to local emissions or to emissions from

TABLE 5.1 High NO_2 Values Observed in the Vicinity of Los Angeles, 1975-1977

Distance East of Downtown LA, (mi)	Site	No. of Hourly* Rdgs > 0.20 ppm	Max. Conc.*
-12	LA Gault Street	205	.35
-10	LA Westwood	628	.62
-5	Lennox	297	.40
-2	Burbank	386	.48
0	LA San Pedro	633	.62
5	Lynwood	163	.39
10	Pasadena	526	.46
14	Temple City	264	.47
15	Whittier	386	.62
23	La Habra	212	.47
23	Azusa	166	.38
32	Pomona	231	.41
35	Chino	47	.38
38	Upland	13	.34
38	Upland	38	.30
38	Upland	17	.27
52	Rubidoux	8	.28
52	Rubidoux	5	.26
55	Riverside	82	.35
55	Riverside	31	.30
52	Fontana	4	.24
55	San Bernardino	11	.25
67	Redlands	9	.29

* Numbers have not been adjusted downward to account for 10-17% overestimation resulting from calibration method used during 1975-77.

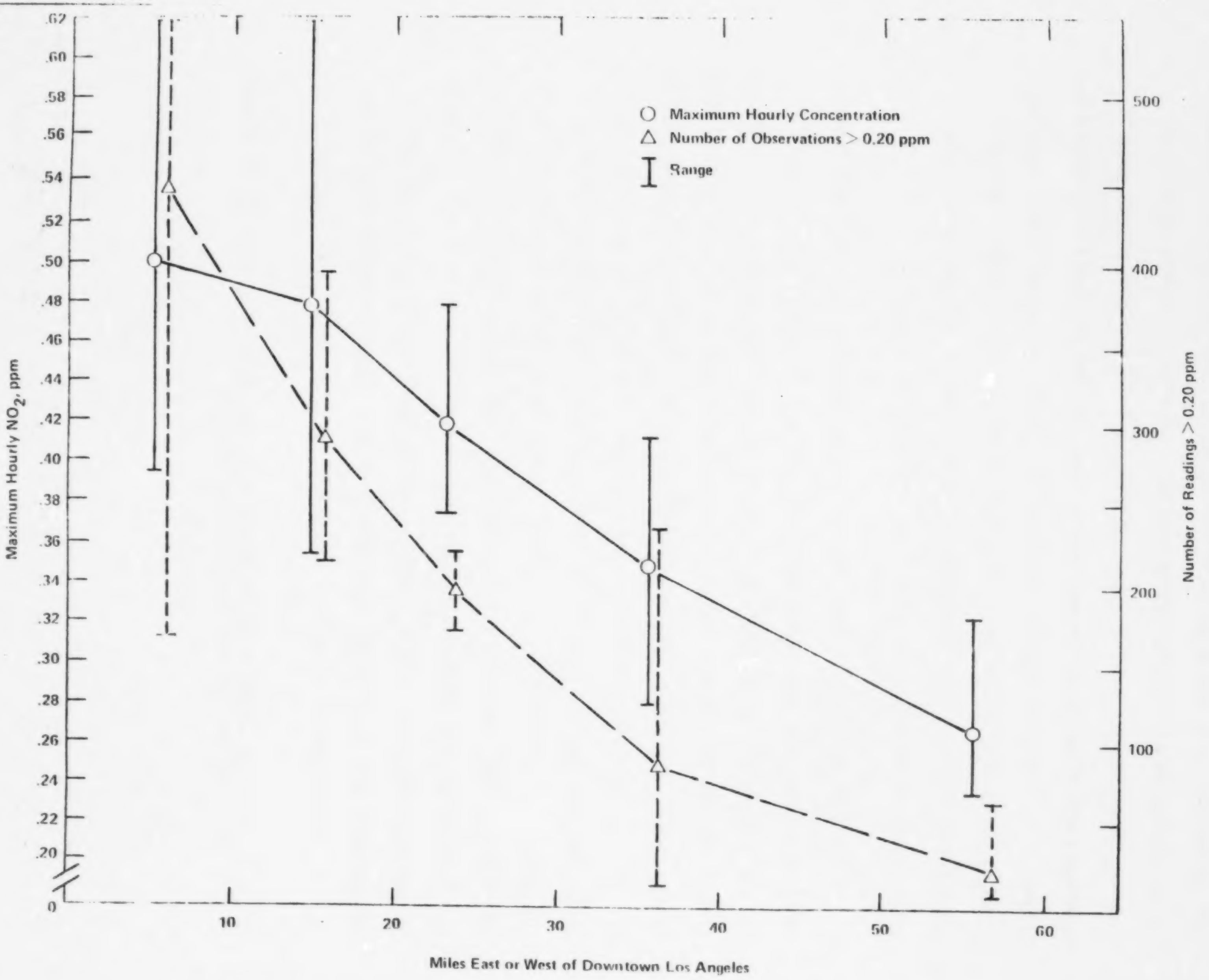


Figure 5.1 Gradients in Maximum Hourly NO_2 Observed in the Los Angeles Basin.

cities which are a few tens of miles upwind. For example, in Figure 5.2, an NO_2 peak corresponds with increases in CO and O_3 during the mid-afternoon, whereas NO concentrations remain low throughout the day. The site (El Toro) is not one which is characterized by high local emissions. The NO_2 peak* in this case is apparently attributable to transport. In contrast, the NO_2 peaks illustrated for October 2-4, 1975 in Riverside, California in Figure 5.3 suggest local formation of NO_2 attributable to synthesis (morning) and titration (evening). In the Los Angeles area data base, instances of local generation of NO_2 in outlying areas appear to be much more common than instances of transport.

Because of the role of local NO_x and VOC emissions in the Los Angeles area, Figure 5.1 may imply that transport of NO_2 is more important than it actually is. For this reason, it is informative to review NO_2 gradients observed in the St. Louis area during the RAPS study. Table 5.2 and Figure 5.4 show that, as in Los Angeles, maximum hourly NO_2 concentrations diminish with increasing distances from downtown St. Louis. The difference is that the gradient is somewhat sharper (e.g., within 40 km, maximum, C_{99} and C_{50} concentrations are less than half those observed downtown). A second difference is that the NO_2 levels in and near St. Louis are consistently lower than those in Los Angeles. This second difference is probably attributable to more favorable meteorology and somewhat less extensive emissions in the St. Louis area. The C_{99} and C_{50} values shown in Figure 5.4 approach values which are considerably less than 0.10 ppm. Although maximum NO_2 concentrations 50 km from St. Louis are about 0.08 ppm, the infrequency with which

---

* The NO_2 concentrations shown in Figure 5.2 need to be reduced by 10-17 percent, as a result of the calibration procedure utilized.

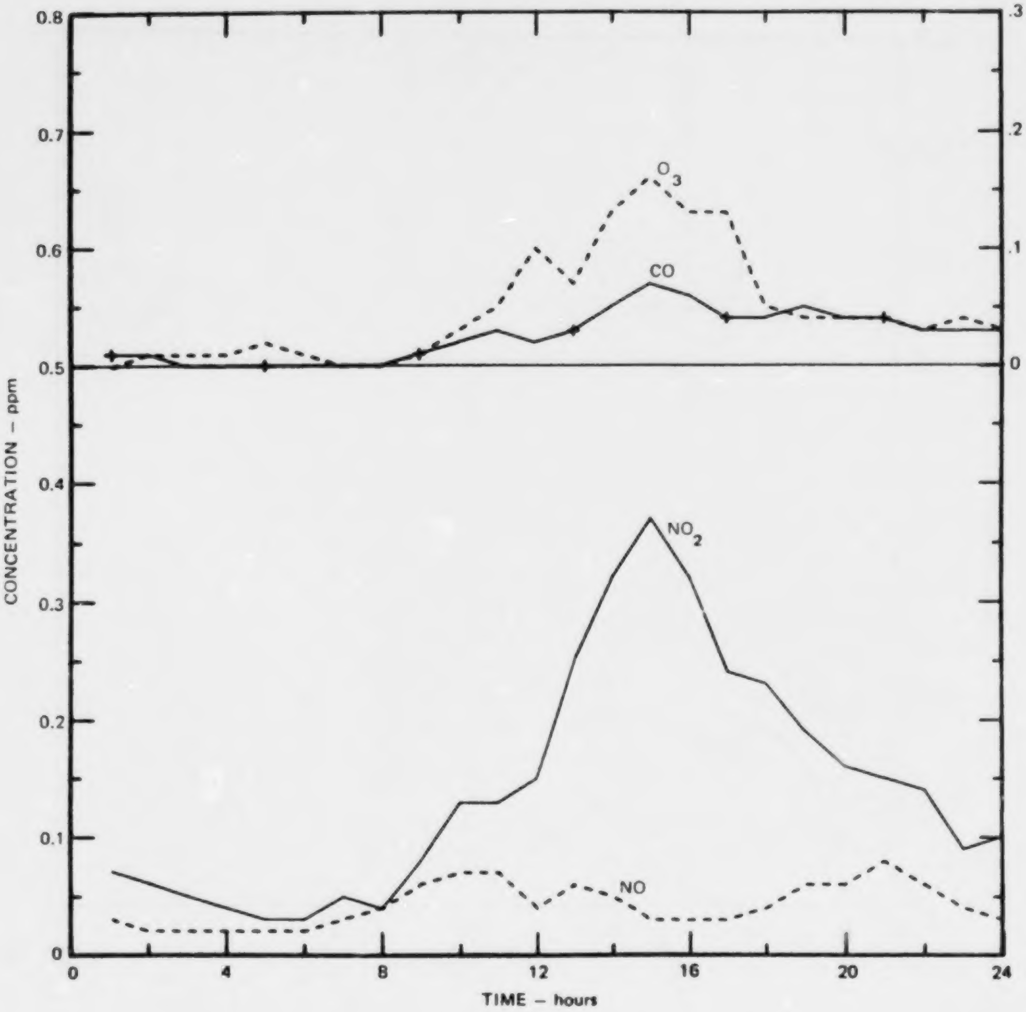


Figure 5.2 Example of NO_2 transport at El Toro station on January 25, 1975. CO has been scaled by 0.01.

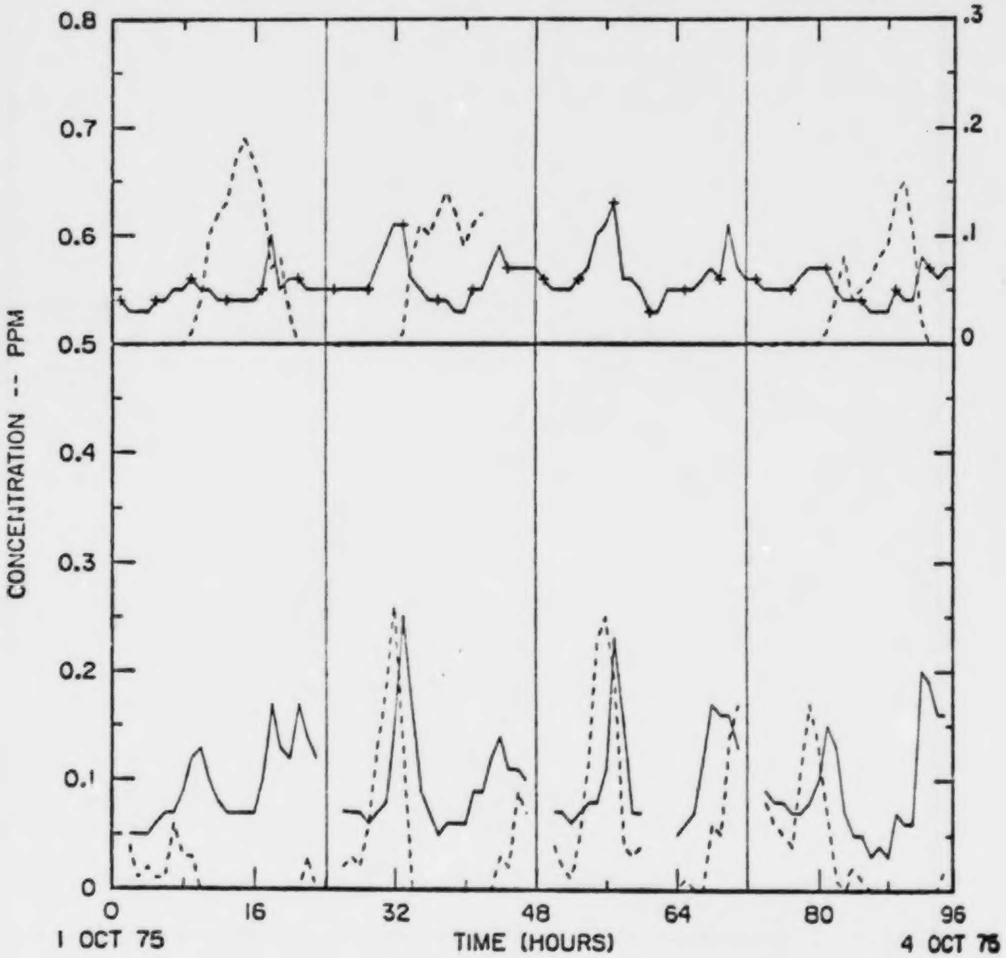


Figure 5.3 Pollutant plots for Riverside, October 1-4, 1975.

Upper panel: O_3 (-----), CO (+—+—), and SO_2 (——); CO concentration scaled by **0.01**
Lower panel: NO (-----), NO_2 (——) (Colorimetric)

TABLE 5.2 Spatial Distribution of Hourly NO_2 Concentrations in the RAPS Network, 1976

Site	Distance From Center City (km)	Valid Hours	Maximum Conc.(ppm)	C_{99} (ppm)	C_{50}
101	0	6147	.256	.08	.026
102	≤ 10	6187	.194	.09	.031
103	≤ 10	5115	.163	.12	.020
104	≤ 10	5353	.156	.07	.024
105	≤ 10	4554	.186	.07	.026
106	≤ 10	5872	.245	.09	.029
107	≤ 10	6164	.191	.08	.029
110	≤ 10	7180	.140	.06	.015
111	≤ 10	6446	.223	.07	.022
112	≤ 10	6105	.169	.08	.025
108	10-20	6322	.155	.06	.014
109	10-20	6846	.154	.06	.010
113	10-20	5292	.266	.09	.022
114	10-20	7057	.162	.08	.012
117	10-20	6348	.082	.05	.008
118	10-20	6640	.079	.05	.009
119	10-20	6189	.192	.06	.015
120	10-20	6420	.192	.07	.016
115	20-30	7048	.090	.05	.009
116	20-30	6371	.081	.05	.009
121	20-30	5998	.168	.07	.008
123	30-40	6012	.087	.04	.005
124	40-50	6481	.082	.04	.003
122	50-60	6966	.086	.04	.002
125	50-60	6527	.067	.03	.001

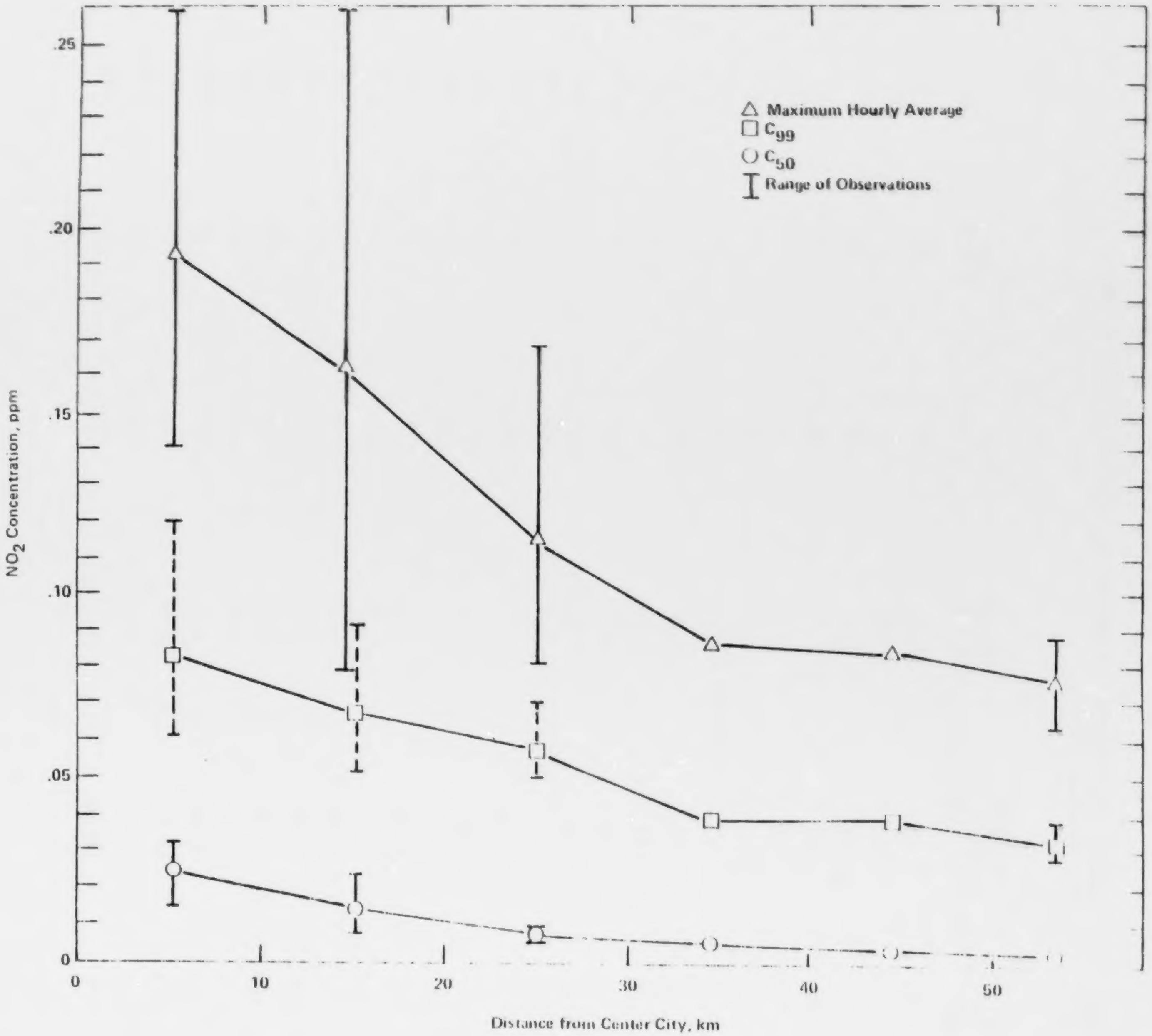


Figure 5.4 Gradients in Maximum NO_2 Concentrations Observed During the St. Louis RAPS

transport appears to be the primary cause of high NO_2 in outlying areas in Southern California suggests that it is unlikely that high NO_2 observed in a city is significantly impacted by NO_2 transported from a city more than 50-70 miles away. This hypothesis is further examined in Section 5.2 where NO_2 observations made in rural and remote areas are presented.

5.2 Levels of NO_2 Reported in Rural Areas

Concentrations of NO_2 observed in several recent field studies are summarized in Table 5.3. As with the data collected in outlying areas of St. Louis, ambient NO_2 concentrations in rural areas are almost always (C_{99}) very low. With rare exceptions, even the maximum hourly NO_2 concentrations observed are less than 0.05 ppm.

Table 5.4 shows mean $NO/NO_2/NO_x$ concentrations observed in remote areas. The distinction between "remote" and "rural" is that a remote location is far from populated areas. Hence, its pollutant levels are not expected to be influenced by anthropogenic sources.[3] A rural site, on the other hand, is one which is more likely to be impacted by transport from urban areas. Rural sites may include small communities which may generate limited amounts of pollutants, but no major sources.[3]

In comparing Table 5.4 with the C_{50} values in Table 5.3, one sees that there are, most probably, measurable amounts of residual NO_2 present at rural sites. However, these concentrations are usually an order of magnitude of more below 0.10 ppm.

TABLE 5.3 NO_2 Observed at Rural Sites

Site	Sampling Period	Approximate Max. NO_2 Conc. (ppm)	C_{99}	C_{50}
Kane, PA	June 26-September 30, 1973	.045	.020	.010
Coshocton, OH	June 26-September 30, 1973	.060	.035	.015
Lewisburg, W. VA	June 26-September 30, 1973	.085	.030	.010
Wilmington, OH	June 14-August 31, 1974	.045	.035	.005
McConnelsville, OH	June 14-August 31, 1974	.035	.020	.005
Wooster, OH	June 14-August 31, 1974	.045	.035	.005
McHenry, MD	June 14-August 31, 1974	.030	.020	.005
Dubois, PA	June 14-August 31, 1974	.035	.020	.005
Bradford, PA	June 27-September 30, 1975	.020	.015	.005
Creston, IA	June 27-September 30, 1975	.010	.010	.005
DeRidder, LA	June 27-October 31, 1975	.025	.010	.005
Wolf Point, MT	June 27-September 30, 1975	.025	.010	ND
Simsbury, CT	July 15-August 21, 1975	.023	NA	NA
Montague, MA*	August 1-December 31, 1977	.073	.016	.007
Duncum Falls, OH*	August 1-December 31, 1977	.043	.018	.008
Giles County, TN*	August 1-December 31, 1977	.055	.024	.011
Lewisburg, W. VA	August 1-December 31, 1977	.028	.009	.004

+ Mean daily maximum, approximately equal to C_{99} for the sampling period shown
++ Mean rather than C_{50}
ND Not Detectable
NA Not Available
* SURE data provided courtesy of EPRI

TABLE 5.4 Concentration of Nitrogen Oxides Observed in Clean Remote Areas

Location	Concentration (ppb)			Measurement Method	Date of Measurement	Reference	Remarks
	NO_x	NO	NO_2				
Laramie, Wyoming	0.1 - 0.4	0.01 - 0.05		Chemiluminescent	Summer 1975	Drummond (1977)	
Fritz Peak, Colorado			<0.1	Absorption spectroscopy	Fall 1974; Summer-Spring, 1975-1976	Noxon (1975, 1978)	
Fritz Peak, Colorado	0.2 - 0.5			Chemiluminescent	Sep 1977	Ritter et al. (1978)	
Northern Michigan	0.3 - 0.5			Chemiluminescent	Jun 1977	Ritter et al. (1978)	10-day average
Tropical Areas		0.1 - 0.5	0.2 - 0.4	Saltzman	1965-1966	Lodge and Pate (1966); Lodge et al. (1974)	Under forest canopy
		0.3 - 0.4	0.3 - 0.5			Lodge and Pate (1966); Lodge et al. (1974)	Above forest canopy
		0.3 - 0.7	0.3 - 0.6			Lodge and Pate (1966); Lodge et al. (1974)	River bank
		0.3 - 0.7	0.3 - 0.5			Lodge and Pate (1966); Lodge et al. (1974)	Seashore and maritime
Ireland		≤0.2	0.2 - 1.5	Chemiluminescent	Jul-Nov 1974	Cox (1977)	Maritime. Maximum hourly averages ranged from 0.3 to 5.0 ppb.

5.3 Chemistry of Transported NO_x

Information presented in the two previous sections indicates that only very low concentrations of NO_2/NO_x are likely to be transported over substantial distances. In this section, observations concerning chemistry of NO_x as it is transported are briefly described. This information is pertinent for two reasons:

1) it provides an upper limit estimate of how far high concentrations of NO_2 may be transported under certain conditions;

2) it brings into better focus the interrelationships between transported NO_x and transported ozone.

In discussing chemical stability, it is more appropriate to consider stability of NO_x ($NO + NO_2$) rather than NO_2. The reason for this is that within a well mixed urban plume subject to photochemical reactions, NO is rapidly converted to NO_2 and vice versa. Stability of NO_x, however, allows consideration to be given not only to NO_2, but to NO available to rapidly replenish any lost NO_2.

Recently, a number of efforts have been made to estimate the chemical stability of ambient NO_x and to determine its reaction products.[16, 17,18, 3] Measurements made downwind of Los Angeles have been used to infer NO_x decay rates of 2-16 percent/hour, with typical conversion rates being about 10 percent/hour or slightly less. However, it has been hypothesized that such estimates may underestimate the conversion rate of NO_x. This hypothesis follows from the manner in which the conversion rate estimates are made and from the fact that there is a continuing infusion of fresh NO from cities downwind of Los Angeles. The hypothesis that a 10 percent/hour NO_x conversion rate may be too low has been tested in two sets of experiments. The first set was made downwind of Phoenix, a city with relatively little surrounding development. Surprisingly, NO_x conversion rates of only about 5 percent/hour were observed in these experiments.[18] More recent experiments conducted in the Boston plume, as it is transported over the ocean, have indicated NO_x conversion rates of 14-24 percent/hour, which average about 17 percent/hour.[18] Corresponding lifetimes for NO_x are shown in Table 5.5.

All of the chemical lifetimes in Table 5.5 are based on experimental data obtained on sunny days in photochemically active urban plumes. It is not possible to draw definitive conclusions about NO_x lifetimes at night, outside of urban plumes or under other meteorological conditions, except to say chemical lifetimes of NO_x may be somewhat longer under conditions which are not conducive to photochemical reactions. However, data presented in Chapters 3.0 and 4.0 imply that NO_2 is at its highest within urban plumes and in sunny weather. This allows for some speculation about maximum distances for transport of high NO_2 concentrations. If one is willing to assume that daytime NO_x conversion rate is at least 5 percent/hour and most probably greater than 10 percent/hour, maximum travel distance of significant NO_2 is probably limited to 100-300 miles.* This estimate represents a maximum one, because the impact of atmospheric dilution is not taken into account. It is clear from the minute concentrations of NO_x reaction products (mostly PAN and nitric acid) that dilution is the primary means by which ambient NO_x is reduced. In addition, the information presented in Sections 5.1 and 5.2 also support the assertion that dilution is the most important factor causing the distinct differences observed between NO_2 concentrations in urban and rural areas.

---

* This estimate was arrived at by assuming a resultant wind velocity of 10 mph prevailing throughout the chemical lifetime of NO_x as reported in Table 5.5. Nighttime decay rate is assumed to be 0 percent/hour in these calculations.

TABLE 5.5 Chemical Stability of NO_x Corresponding to Observed Conversation Rates

Conversion Rate (%/hr)	Half Life[†] (hr.)	Lifetime* (hr.)
2	35	50
5	13	19
10	6	9
14	5	7
17	3.7	5.3
24	2.5	3.6

* Lifetime is commonly assumed to be the time required for a pollutant to decay to $^1/e$ or to 37% of its original concentration

[†] Time required for a pollutant to decay to 50% of its original concentration

A discussion of transport of NO_x is not complete without mention of the interrelationships with transport of ozone. There are really two issues which need airing:

1) What is the impact of ozone, transported from upwind areas, on NO_2?

2) What is the impact of transported NO_x on downwind concentrations of ozone?

The impact of transported ozone on NO_2 can be seen by referring once again to Figure 5.3 (page 40). The dashed lines in the upper set of panels in this figure indicate that, during the period in question, ozone concentrations on October 1 and 4 reached Riverside, California from points further west about 4 p.m. This ozone then reacts with local NO emissions resulting in NO_2 concentrations approaching 0.20 ppm in the early evening. This, of course, is an example of the titration phenomenon discussed in Chapter 3.0. Control programs resulting in the reduction of transported ozone should therefore reduce peak NO_2 concentrations resulting from titration of NO with ozone when ozone is the limiting factor.

The impact of transported NO_x on downwind ozone is a difficult issue. Formation of ozone from NO_x and NMOC is not the result of a chain-ending reaction (i.e., in addition to ozone, NO_x and additional organic radicals are also formed as by-products which, in turn, can recombine several more times to form more ozone). Therefore, concentrations of NO_x well below 0.10 ppm are sufficient to sustain synthesis of ozone in excess of the NAAQS for ozone. This observation, in turn, leads to the following question: should NO_x emissions be controlled even though they pose no threat in terms of unacceptably high concentrations of NO_2?

At this point, control agencies are confronted with an as-yet-to-be-resolved dilemma. Model simulations, as well as ambient data, show that the most immediate effect of NO emissions is to suppress ambient levels of ozone within the vicinity of the emissions. Since areas with greatest emissions are usually those in which the greatest number of people reside, there is a concern that aggressive programs to curtail NO_x emissions in such areas may increase population exposure to high concentrations of ozone. Counterbalancing these arguments are those (briefly alluded to above) which suggest that the availability of NO_x may aggravate highest ozone concentrations in downwind areas and that reduction of available NO_x in rural areas may be needed to curb pervasive ozone problems reported in the northeastern U.S. and elsewhere. There is some support for the argument that NO_x emissions aggravate peak ozone concentrations downwind which can be found in the Los Angeles trend data.[19] Arguments have also been made that NO_x should also be controlled in order to reduce other oxidants as well (e.g., PAN).

Both the arguments for and against aggressive controls of NO_x emissions appear plausible. Unfortunately, the state-of-the-art has not sufficiently advanced to allow quantitative tradeoffs to be made. Indeed, much of the research cited in this section, as well as other work, has been conducted for the purpose of developing information needed to make these quantitative tradeoffs. It is not likely, however, that the problem will be satisfactorily resolved within an immediate time frame. Therefore, the foregoing information has been presented to alert control officials to the possibility that more stringent NO_x controls than those implied by any hypothetical NAAQS for NO_2 may be needed.

5.4 Implications

1. Despite the fact that NO_2 is a secondary pollutant, it does not appear that high concentrations are transported over great distances. Highest concentrations of NO_2 occur near areas with high NO_x emission density. While it is possible for high NO_2 to persist throughout the night (i.e., the carryover phenomenon), comparison of urban, suburban and rural data implies that such persistence results from poor dispersion in the vicinity of source-intensive areas, rather than as a result of transport from afar.

2. Chemical decay rates of NO_x (i.e., NO + NO_2) serve to provide an upper limit estimate for transport of appreciable concentrations of NO_2. Although there is some spread in the data, decay rates of about 10 percent per hour appear to be representative of daytime observations within an urban plume. Assuming a resultant wind speed of 10 mph, an upper limit for transport of high concentrations of NO_x of about 100-300 miles is estimated.

3. Available urban concentration gradient data, as well as rural data however, suggest that transport of NO_2 approaching 0.10 ppm is, in fact, limited by atmospheric dilution. In the RAPS network, for example, peak hourly NO_2 is reduced from .25 ppm to .08 ppm within 50 km of downtown. Rural data indicate that NO_2 concentrations seldom exceed .03 ppm. Therefore, if one is primarily concerned with an hourly NO_2 concentration of 0.20 ppm or more, impact of long range transport of $\underline{NO_2}$ can ordinarily be ignored in the design of control strategies for NO_2.

4. Use of graphs plotting diurnal concentrations of NO_2, NO, O_3, CO and SO_2 may be useful in identifying whether an observed high concentration of NO_2 in a downwind area is due to transport of NO_2. Using such a procedure, high NO_2

observed in areas downwind of Los Angeles were frequently found to result primarily from the titration of locally generated NO with ozone which was transported from upwind sources. Hence, programs to reduce transported ozone may also reduce peak NO_2 generated in downwind areas under some conditions.

5. Principal reaction products of NO_x are PAN and nitric acid. These pollutants exist in minute quantities in the atmosphere. Under some conditions, PAN can regenerate NO_2. In addition, comparison of rural with remote data indicates that low concentrations of residual NO_2 can survive over considerable distances. Unfortunately, it only requires very small quantities of NO_x (well below 0.10 ppm) in the presence of NMOC to sustain ozone concentrations above the NAAQS for ozone. This suggests that more stringent requirements for controlling NO_x emissions may be needed to meet the ozone NAAQS than to avoid unhealthy exposures to NO_2. Unfortunately, quantitative tradeoffs between possible increases in ozone levels in the vicinity of sources of NO versus possible decreases in ozone levels observed downwind of sources of NO cannot be made at the present time. While information is being obtained to develop better tools to quantify the impact of NO_x controls on ozone levels in rural areas, it is probably a good idea to minimize any increases in NO_x emissions as a part of ozone SIP's.

6.0 RELATIONSHIPS BETWEEN NO_2 AND ITS PRECURSORS

Previous chapters have established that ambient NO_2 is primarily a "secondary" pollutant. It has also been noted that nitric oxide (NO), non-methane organic compounds (NMOC),* and ozone (O_3) play important roles in the formation of NO_2 in ambient air. The purpose of this chapter is to discuss relationships between NO_2 and these other pollutants in greater detail. Three means have been used to examine relationships between NO_2 and its precursors: (1) smog chamber experiments, (2) empirical models, and (3) chemical kinetics models. Section 6.1 discusses the results obtained using each of these three approaches. Section 6.2 then summarizes the implications of these results on the design of control strategies to reduce ambient levels of NO_2.

6.1 Relations Among NO_2 and Precursors

Although it is obvious why peak and average NO_2 could be sensitive to NO_x levels, it may not be instinctively clear why NO_2 should be affected by ambient levels of NMOC. Reducing ambient NMOC reduces the concentration of organic radicals which serve to oxidize NO to NO_2. The resulting lower concentrations of organic pollutants therefore delays the formation of NO_2. Such a delay allows greater dilution of NO to occur prior to oxidation. The end result is lower concentrations of NO_2 when the NO finally does get oxidized.

---

* In the discussion in Chapter 6.0, the term NMOC is used rather than VOC because the smog chamber, empirical and kinetics model evidence all deal with ambient levels of pollutants rather than emissions. The terms HC and NMHC (non-methane hydrocarbon) are sometimes used because they are used in the primary references. In this discussion, NMOC, HC and NMHC may be assumed to be synonymous.

6.1.1 Smog Chamber Experiments

A smog chamber is a transparent container into which known concentrations of organic pollutants (NMOC) and NO_x are injected. The resulting mixture is then irradiated with ultraviolet light (using either sunlight or an artificial source). The resulting concentrations of NO_2 and other secondary pollutants can then be observed. By varying the initial concentration of NO_x or NMOC and keeping everything else constant, the sensitivity of maximum hourly NO_2 concentrations to changes in these precursors can be ascertained.

The results of six sets of smog chamber experiements have been recently summarized by Trijonis.[20] Figures 6.1 - 6.4 summarize the dependence of peak NO_2 on initial NO_x concentrations in these experiments. As shown in Figures 6.1 - 6.4, despite the wide variety of experimental conditions, the relationship between peak NO_2 and NO_x can be approximated by a straight line (i.e., is linear). The slope of the line is generally slightly less than 1:1. Similar relationships were found between initial NO_x and mean NO_2.[20]

Smog chamber data are more ambiguous with regard to the dependence of NO_2 on initial NMOC concentrations. Most of the data indicate that, within the range of observations encompassed by the experiment, there is a weak relationship between peak NO_2 and initial NMOC concentrations. For example, the experiments cited indicate that reducing NMOC by 50 percent results in a reduction in peak NO_2 ranging from 0-25 percent. The experimental evidence reported is inconclusive regarding the direction of change in mean NO_2 corresponding with a reduction in NMOC. The results of the smog chamber studies are summarized in Table 6.1.

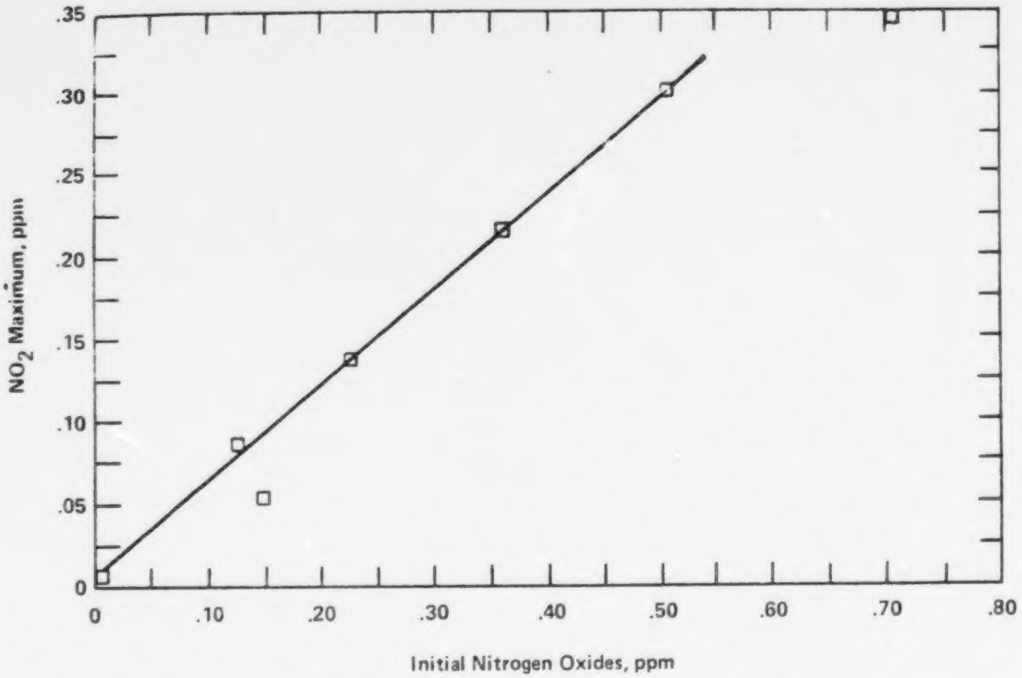


Figure 6.1 Nitrogen Dioxide Maximum Concentration vs. Initial Oxides of Nitrogen (means of several experiments) UNC Study.

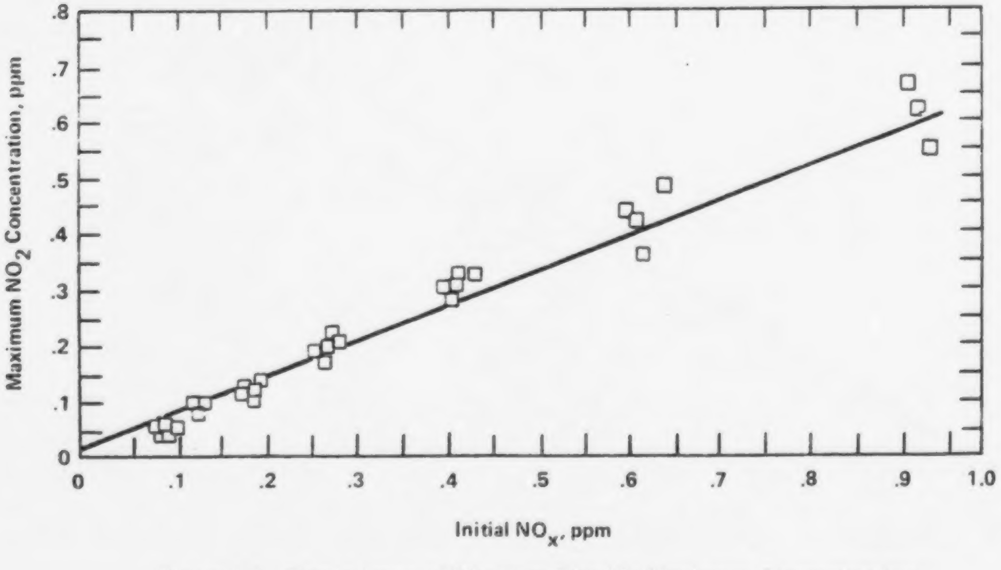


Figure 6.2 Dependence of Nitrogen Dioxide Maximum Concentration on Initial Nitrogen Oxides, Bureau of Mines Study.

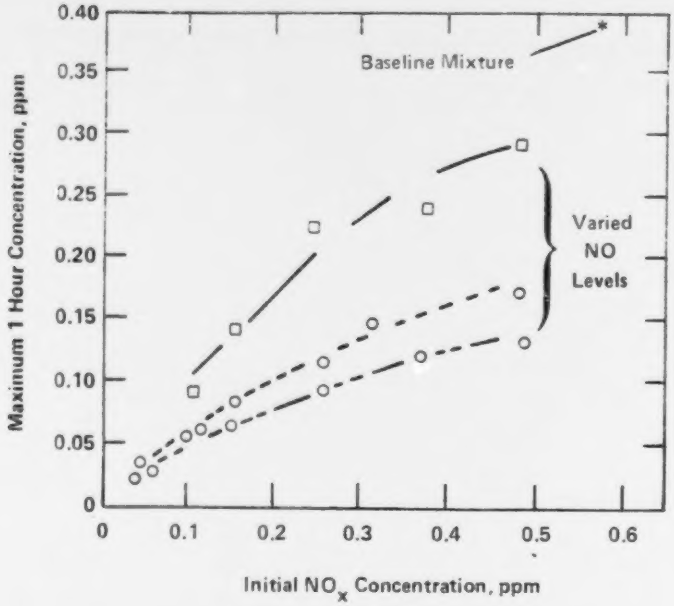


Figure 6.3 Maximum One-hour Nitrogen Dioxide Concentration Produced from Irradiation of Multicomponent Hydrocarbon/NO_x Mixtures, General Motors Study.

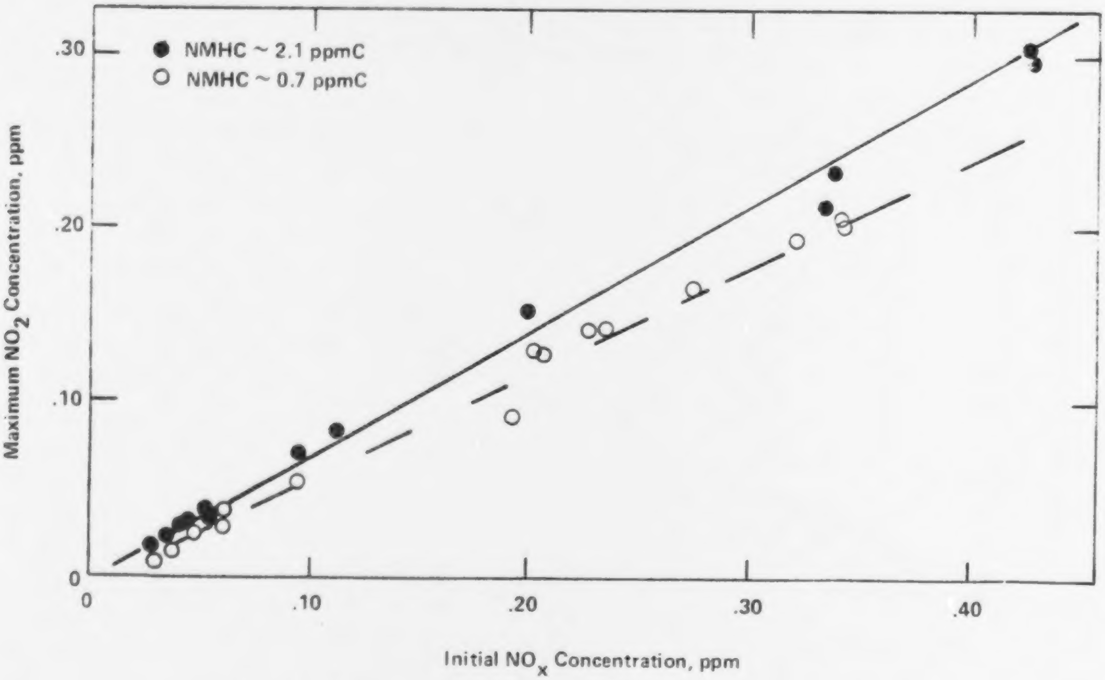


Figure 6.4 Maximum Nitrogen Dioxide Concentration as a Function of Initial NO_x for Two Initial Hydrocarbon Levels, UC Riverside Study.

TABLE 6.1 Summary of Conclusions from Smog Chamber Experiments

CHAMBER STUDY	MAXIMAL NO_2 Dependence on NO_x	MAXIMAL NO_2 Dependence on HC	AVERAGE NO_2 Dependence on NO_x	AVERAGE NO_2 Dependence on HC
University of North Carolina	Proportional or slightly less than proportional	50% HC control reduces maximal NO_2 by 10% to 20%	Proportional or slightly less than proportional	Uncertain, 50% HC control may decrease average NO_2 by 20% or may increase average NO_2
Bureau of Mines	Proportional	No effect	Proportional	50% HC control increases average NO_2 by 10% to 30%
General Motors	Slightly less than proportional	50% HC control reduces maximal NO_2 by 25%	Proportional to slightly less than proportional	No effect
UC Riverside	Proportional	50% HC control reduces maximal NO_2 by 10% to 15%	Proportional	No effect
HEW, Auto Exhaust	- - - - - - - -	- - - - - - - -	Proportional	No effect
HEW, Toluene	- - - - - - - -	- - - - - - - -	Proportional	No consistent effect

SOURCE: Reference 20

6.1.2 Empirical Relationships from Ambient Data

The second approach used to determine relationships between NO_2 and precursors has been to examine ambient data for existing statistical relationships. Empirical models based on these relationships have then been constructed. This approach has been tried at eight locations -- four in the Los Angeles basin, two in Houston and one each in Denver and Chicago.[20,21] For each site, a stepwise regression approach was used to derive the coefficients in Equations (6.1) and (6.2). For peak NO_2 values occurring between 6:00 a.m. and 4:00 pm:

$$\begin{array}{l}\text{Daytime}\\ \text{Peak } NO_2\end{array} = A + B_1[NO_2]_5 + \text{INTNO} \cdot [B_2 + B_3\,[\text{NMHC}] + B_4\,[\text{RATIO}]] \quad (6.1)$$

where A, B_1, B_2, B_3, B_4 = coefficients of regression

$[NO_2]_5$ = NO_2 concentration at 4-5:00 a.m.
[INTNO] = initial NO input (6-9 a.m. NO_x - $[NO_2]_5$)
[NMHC] = 6-9 a.m. non-methane hydrocarbon concentration
[RATIO] = 6-9 a.m. NMHC/NO_x ratio

For peak NO_2 values occurring between 4:00 p.m. and 6:00 a.m.,

$$\begin{array}{l}\text{Nighttime}\\ \text{Peak } NO_2\end{array} = A + B_1[NO_2]_{16} + B_2[\text{NITENO}] + B_3\,[\text{NITENO}][O_3\text{AFT}] \quad (6.2)$$

where

$[NO_2]_{16}$ = NO_2 at 3-4 p.m.
NITENO = initial NO input (4-7 p.m. NO_x minus $[NO_2]_{16}$)
O_3AFT = ozone at 2-4 p.m.

Analogous equations were also developed for average daytime and nighttime NO_2. Data used to derive Equations (6.1) and (6.2) were seasonally disaggregated into summer (April-September) and winter (October-March). As described subsequently, such disaggregation allows further insight into relationships between NO_2 and reduction in NMOC. Hence, Equations (6.1) and (6.2) were derived and applied separately to summertime and wintertime data.

The empirical models derived for six of the eight locations* imply that reductions in NO_x yield slightly less than proportional reductions in peak NO_2, providing all other factors are kept constant. Reductions in average NO_2 are approximately proportional to reductions in NO_x. These results are summarized in Table 6.2.

As with smog chamber data, more ambiguous results were obtained when assessing the impact of reducing NMOC on peak and average NO_2. The results are presented in Table 6.3. According to the data in Table 6.3, there may be a slight benefit as measured by reduced peak NO_2 accompanying NMOC reduction. This effect is practically negligible for mean NO_2. It is interesting to note that the effect of reducing NMOC appears to be somewhat more pronounced in winter than in summer. This is consistent with the hypothesis that since daytime NO_2 peaks occur later during winter anyway, additional efforts to delay NO_2 formation may be more effective.

An important caveat needs to be stated, before the results shown in Tables 6.2 and 6.3 are taken too far. Equations (6.1) and (6.2) do not explicitly take account of meteorological differences. Inclusion of meteorological variables in the relationships may change some of the conclusions, particularly with regard to

---

* The two Houston sites were excluded because of poor fit of the models with nighttime data.

TABLE 6.2 Empirically Estimated Dependence of NO_2 on NO_x Control

Location	Maximum NO_2 50% NO_x Control No Change in NMOC	Mean NO_2 50% NO_x Control No Change in NMOC
Downtown LA	-37%	-45%
Lennox, CA	-40%	-47%
Azusa, CA	-45%	-48%
Pomona, CA	-31%	-43%
Denver, CO	-43%	-55%
Chicago, IL	-50%	-50%
Average	41%	48%

Table 6.3. Estimated Impact of Reducing NMOC on Peak NO_2 Obtained With Empirical Models

Location	Summer Day % Change in Peak NO_2 Accompanying 50% Reduction in NMOC	Summer Day % Change in Ave. NO_2 Accompanying 50% Reduction in NMOC	Winter Day % Change in Peak NO_2 Accompanying 50% Reduction in NMOC	Winter Day % Change in Ave. NO_2 Accompanying 50% Reduction in NMOC
Downtown Los Angeles	-19%	-6%	-25%	-14%
Lennox, CA	-16%	-4%	-10%	- 5%
Azusa, CA	0%	+1%	-15%	- 8%
Pomona, CA	-17%	-9%	-20%	-19%
Denver, CO	- 5%	-7%	- 8%	+ 8%
Chicago, IL	0%	0%	-14%	- 8%
Houston/Mae Dr.	0%	0%	0%	0%
Houston/Aldine	0%	0%	0%	0%
Average	- 7.1%	-3.1%	-11.5%	- 5.8%

NMOC. Trijonis, for example, indicates that the apparent impact of NMOC reduction on NO_2 may be overestimated by the failure of the models to explicitly consider meteorology.[21] Therefore, the significance of the numbers in Table 6.2 and 6.3 is that they agree qualitatively with smog chamber data, rather than provide exact numerical values.

6.1.3 Relationships Derived from Chemical Kinetics Models

A chemical kinetics model is a proposed sequence of chemical reactions. The identity of the reactions and the rates with which they proceed are based on experimental (e.g., smog chamber), as well as theoretical evidence. These models enjoy several advantages over the previously described smog chamber and empirical approaches. These include greater flexibility to test different cases, use of realistic concentrations, and the ability to vary only the parameter of interest (i.e., NMOC or NO_x).

The kinetics model underlying the ozone isopleth model used in EKMA[22] has been modified to express peak hourly NO_2 (rather than O_3) as a function of initial NMOC, NO_x and other factors. The shape of the resulting NO_2 isopleths is more sensitive to assumptions about dilution rate and emission patterns than is the shape of ozone isopleths. It is apparent from Table 6.4 and from Figures 6.5-6.7 that the effectiveness of NO_x and VOC controls in reducing peak NO_2 depends on the prevailing ambient NMOC/NO_x ratio and the levels of NO_2 experienced as well. If 0.30 ppm is assumed to be a "typical" peak NO_2 value, and the NMOC/NO_x ratio is assumed to be 9.5:1,[23] results are similar to those observed in smog chamber experiments and empirically. That is, NO_x reductions result in slightly less than proportional reductions in peak NO_2 and NMOC reductions result in ambiguous changes in NO_2 which are usually slightly beneficial.

Table 6.4. Effect of Separate NO_x and NMOC Reductions on Peak NO_2 Under Various Conditions*

Run	Dilution Rate hr^{-1}	Duration	Subsequent Emissions	Duration	Reduction in NO_2 w. 50% Reduction in NO_x	Reduction in NO_2 w. 50% Reduction in NMOC
1	3%	0800-1500	No	-	-47%	-10%
2	3%	0800-1500	Yes	0600-1600	-50%	0%
3	20%	0800-1500	Yes	0600-1600	-47%	-27%
4	3%	0800-1500	Yes	0600-1400	-50%	0%
5	10%	0800-1500	Yes	0600-1400	-47%	-13%
6	3%	0800-1500	Yes	0600-1600	-50%	0%
7	3%	0800-1500	No	-	-47%	-10%
8	3%	0800-1500	Yes	0800-1800	-50%	0%
9	3%	0800-1500	Yes	0800-1400	-47%	+ 3%
10	10%	0800-1500	Yes	0800-1400	-50%	-13%

* Base Case Assumptions: NMOC/NO_x Ratio = 9.5:1
NO_2 = 0.30 ppm

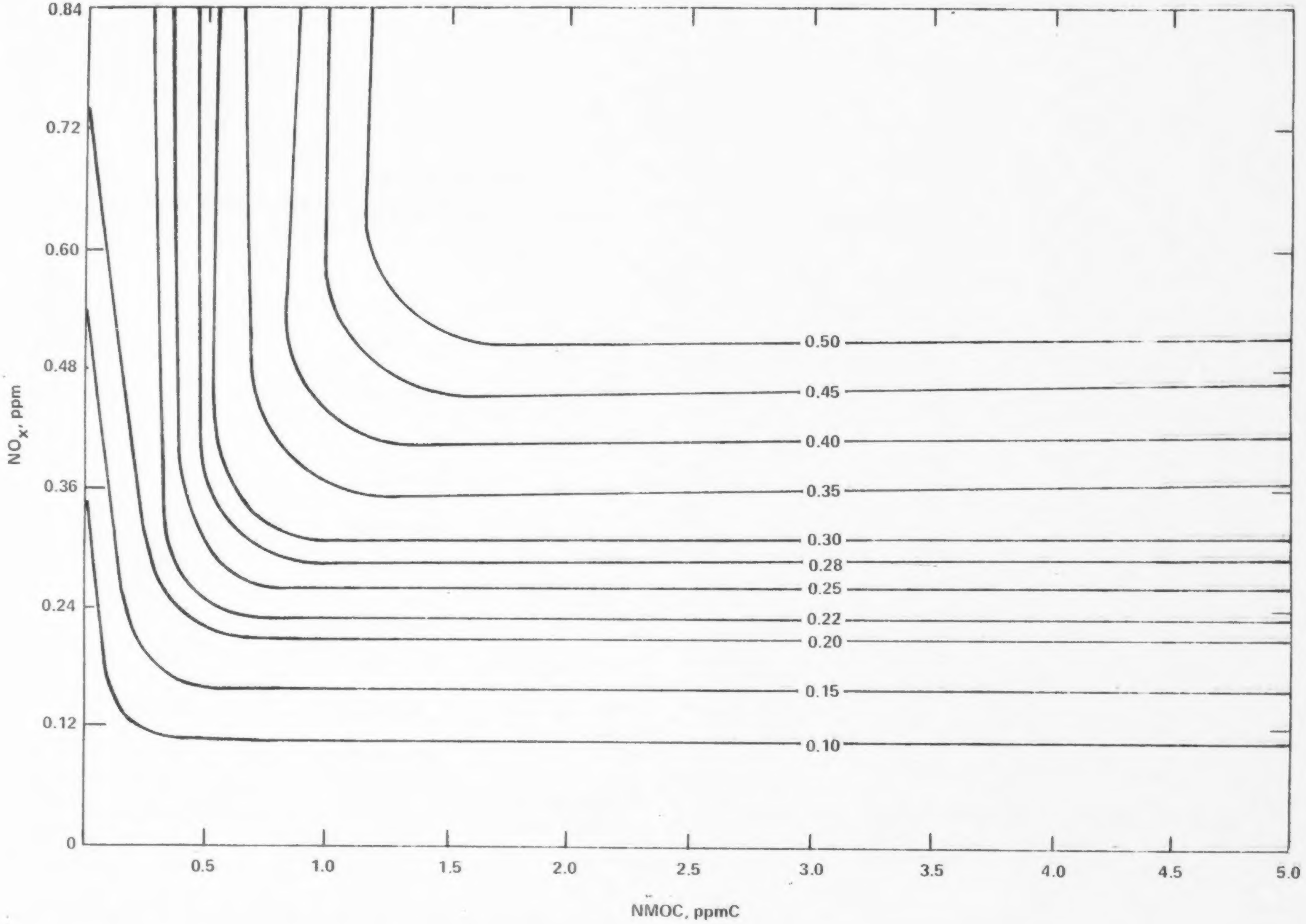


Figure 6.5 NO_2 with 8 Hours of Emissions and 3%/hour Dilution.

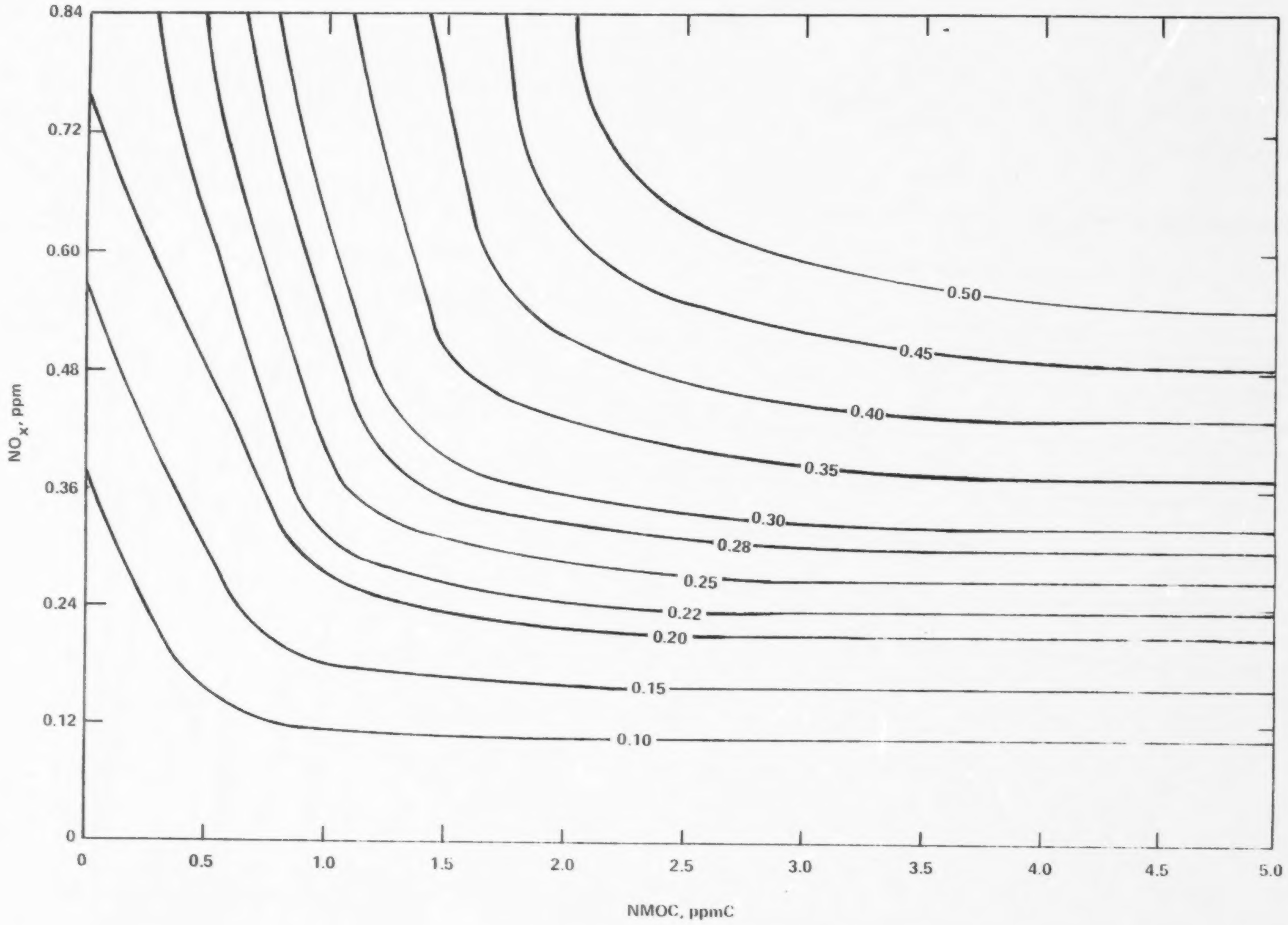


Figure 6.6 NO$_2$ with 8 Hours of Emissions and 10%/hour Dilution.

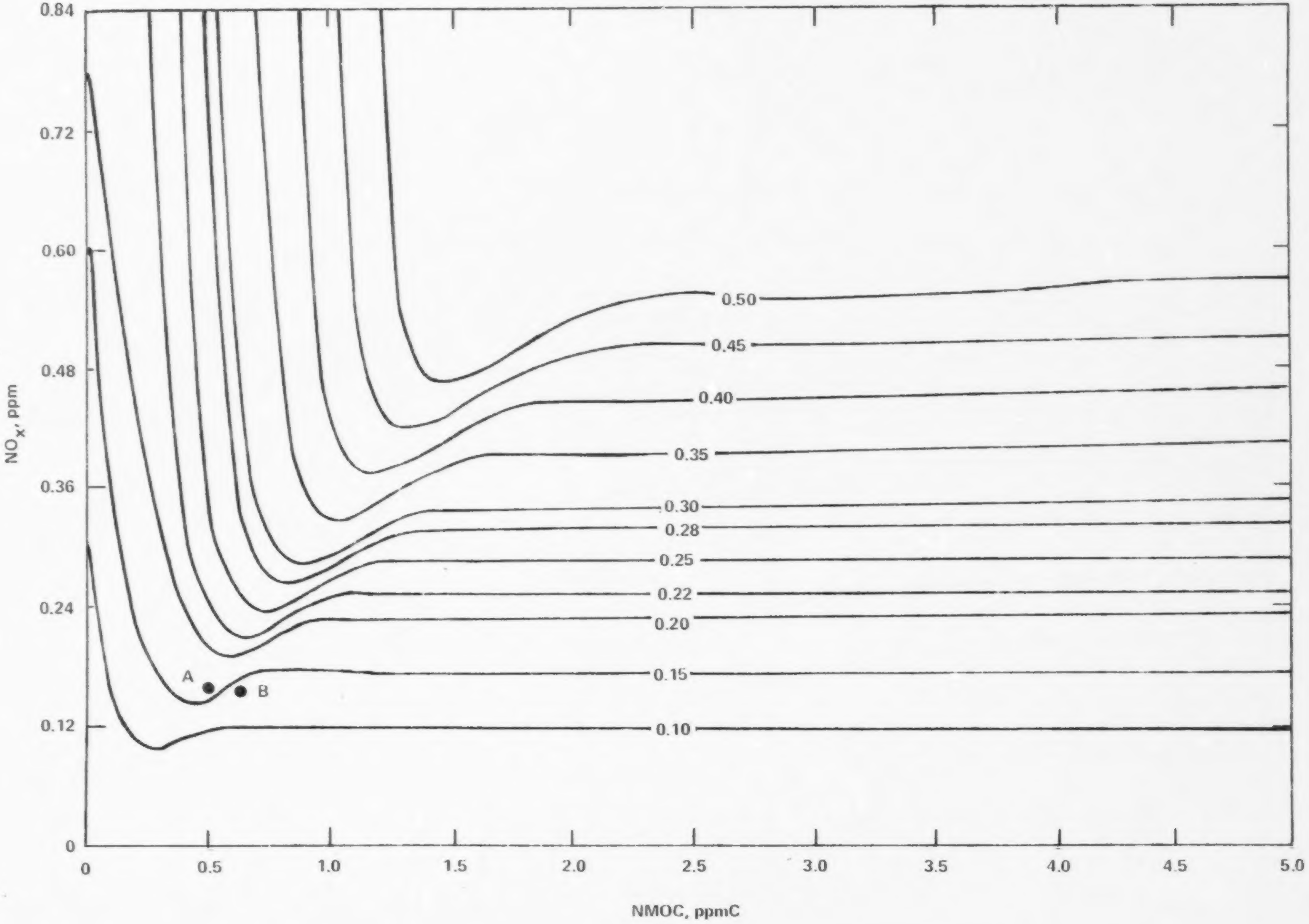


Figure 6.7 NO$_2$, with 10 Hours of Emissions and 3%/hour Dilution.

Examining Figure 6.7 somewhat more closely, one finds the curious result that in some cases decreasing NMOC may increase the peak NO_2! How can this be? The answer can be found by examining in detail how points A and B on Figure 6.7 were derived. This is done by plotting concentrations of NO, NO_2, and O_3 as a function of time on Figures 6.8 and 6.9. Upon doing this, one finds that the lower NMOC level reflected by Figure 6.8 has delayed the NO_2 peak to late in the day, when dilution has been reduced. The ozone peak is similarly delayed. NO emissions occurring late in the afternoon are titrated by the late-forming ozone, resulting in high NO_2 in the early evening. Hence, the strange shape of the isopleths in Figure 6.7 is the result of a different phenomenon (i.e., titration rather than synthesis), causing the highest level of NO_2. These strange looking isopleths only occur when there are substantial NO emissions late in the afternoon.

A second factor that is apparent from Figures 6.5-6.7 is that at very low NMOC/NO_x ratios (less than about 3-4:1) peak NO_2 is much more sensitive to NMOC reductions than to NO_x reductions. Thus, under such conditions the generalizations which have been drawn from smog chamber experiments and empirical models may no longer hold. Because NMOC/NO_x ratios appear to be much higher than this however, previous generalization about the efficacy of NO_x controls versus VOC controls appear valid using the kinetics model as well.

6.2 Implications

1. Smog chamber data, empirical and chemical kinetics models all suggest that reductions in NO_x levels will lead to approximately proportional reductions in both peak and mean concentrations of NO_2. An exception to this may be the case in which peak NO_2 occurs solely as the result of titration reactions with ozone that are limited by the amount of ozone available.

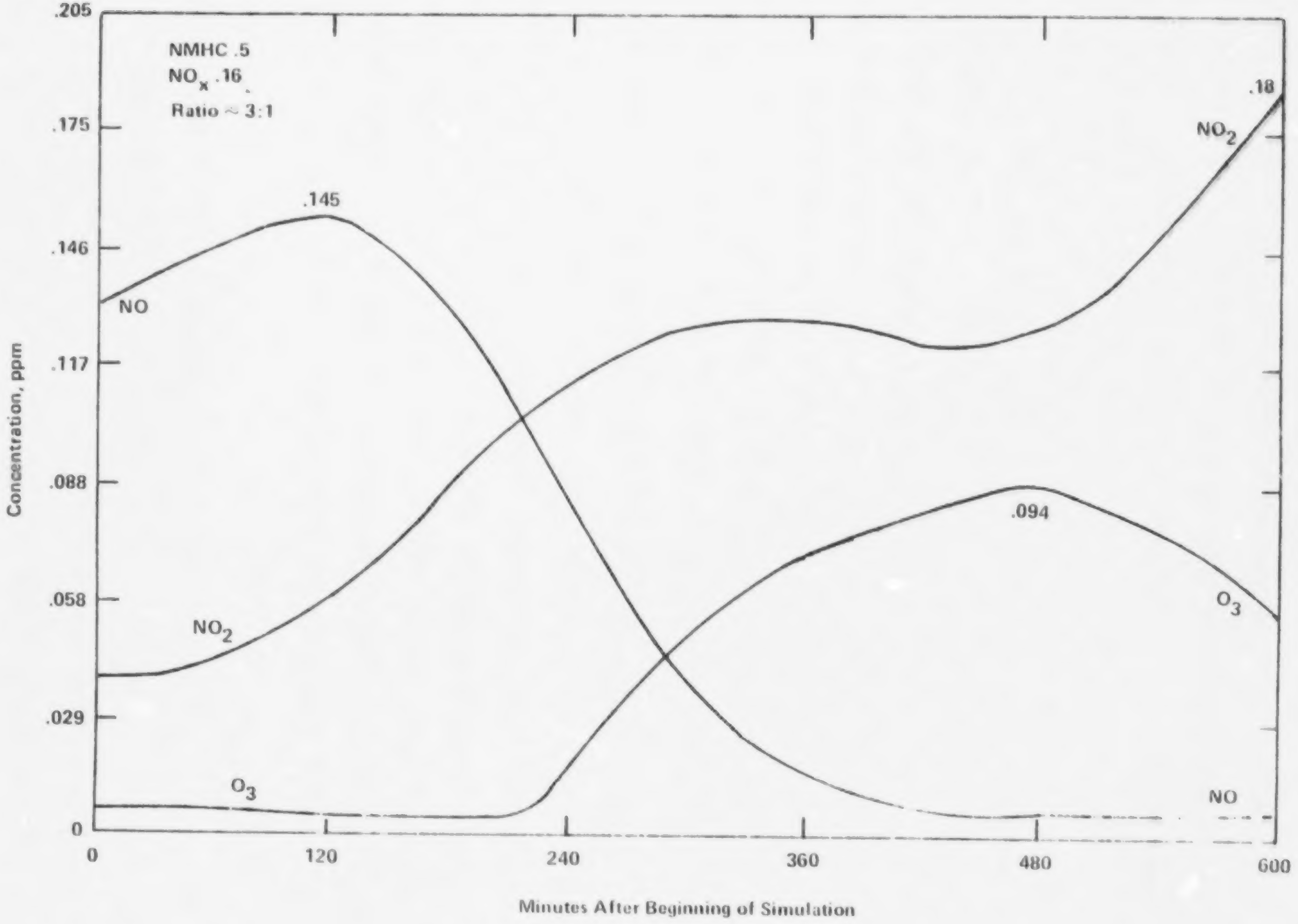


Figure 6.8 NO$_2$, NO and O$_3$ vs. Time for Point A (Figure 6.7).

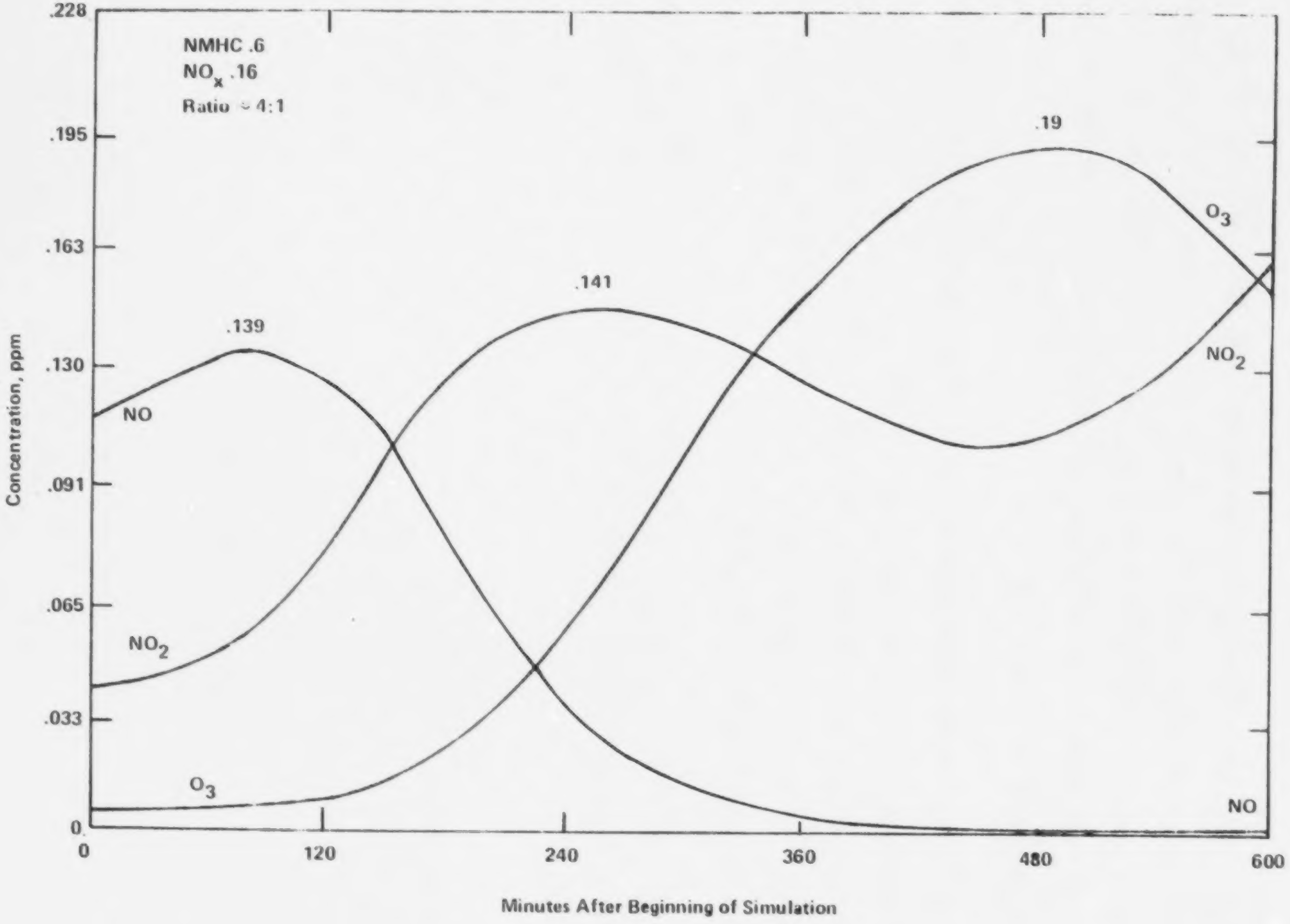


Figure 6.9 NO_2, NO and O_3 vs. Time for Point B (Figure 6.7).

2. The proportionality constant between peak (and mean) NO_2 and NO_x appears to remain approximately the same for a wide variety of $NMOC/NO_x$ ratios, emission patterns and dilution conditions. This implies that the linear rollback model has the potential to serve as a useful means for approximating the impact of NO_x controls on ambient NO_2.

3. The information presented suggests that programs to reduce NMOC levels will not have an appreciable impact on mean NO_2. There may, however, be a small reduction in peak NO_2 accompanying reduction in NMOC under currently prevailing $NMOC/NO_x$ ratios. Data examined imply a reduction in peak NO_2 from 0-20 percent accompanying a 50 percent reduction in NMOC.

4. Because the proportionality constant between peak NO_2 and NMOC reduction appears to be sensitive to a number of factors, the relationship is probably not a linear one.

5. The preceding conclusions appear valid under currently prevailing $NMOC/NO_x$ ratios in urban areas. However, chemical kinetics model simulations suggest that if the prevailing $NMOC/NO_x$ ratio is reduced to very low values (as a result of ozone SIP's), the relative effectiveness of NO_x and VOC controls in reducing NO_2 is different. For example, for ratios of less than about 2-3:1, reduction in peak NO_2 would be more sensitive to further VOC controls than to further NO_x controls.

7.0 IMPACT OF CONTROLLING VARIOUS SOURCE CATEGORIES

Chapter 6.0 has described relationships between peak and mean NO_2 concentrations and NO_x and NMOC precursors. Chapter 2.0 has identified major categories of precursor sources (i.e., stationary, mobile, area, point). Chapter 7.0 presents information which is useful for identifying source categories impacting upon receptor sites. Thus, the concept of source-receptor relationships is introduced. One means for surmising source-receptor relationships is through the interpretation of ambient air quality data. A second approach is through the use of mathematical models.

The first approach is a qualitative one which is useful in justifying assumptions which may have to be made in certain models. The second (modeling) approach is quantitative in that it can be used to estimate reduction in peak or mean NO_2 accompanying specified reductions in precursors. Modeling approaches are discussed in Chapter 8.0.

Prior to reviewing ambient air quality data to better understand source-receptor relationships, it is important to remember that there are likely to be relatively few NO_2 monitoring sites in a given city. Hence, failure to detect an impact of a source category on observed NO_2 concentrations cannot necessarily be used to infer that the category has a negligible impact on NO_2 concentrations throughout the city. Nevertheless, review of ambient air quality data can be extremely useful. Such a review can serve as a means for incorporating source-receptor assumptions in various modeling approaches described in Chapter 8.0. For example, an apparent lack of point source impact at a monitor could justify elimination of that source category from the emission inventory used in applying a model without spatial disaggregation (e.g., proportional rollback) to estimate the impact of precursor controls on peak NO_2 observed at that site. Such a procedure makes it possible for a relatively simple model to explain why an observed improvement in air quality has not accompanied emission reductions from certain source categories. By the same token, control requirements on sources which do impact the monitored air quality data may be less severe.

Review of ambient data collected in the plumes of point sources also serves an important function. The results can be used to justify modeling approaches for considering the major impact of these large sources of NO_x which may occur at locations where there are no monitors.

A third reason for reviewing ambient air quality data in detail is that it serves to emphasize the importance of proper design of a monitoring network. For example, further insight is gained into whether a monitoring site is a representative one. This, in turn, has implications on the use to which the data are put. It would not be suitable, for example, to devise a citywide emission control strategy on the basis of monitoring data which clearly reflected the impact of a single large nitric acid plant.

Two procedures have been used to draw inferences about contributions of various source categories to observed peak NO_2 concentrations. These procedures entail the use of (1) tracer data and (2) peak-to-mean ratios. Results and inferences of each of these procedures are described in Sections 7.1 and 7.2, respectively. More detailed observations of point sources and the resulting implications are described in Section 7.3. Finally, the implications of the findings reported in this chapter to the design of control strategies are summarized in Section 7.4.

7.1 Tracer Approaches

A tracer approach is one which takes advantage of the correspondence between emissions of NO_x and other pollutants emitted by different source categories. For example, suppose emissions from source category A contain pollutant "a," while emissions from category B do not contain "a" but contain pollutant "b" instead. Further, source category A's emissions do not contain pollutant "b." In such a case, detection of "a" by a monitor, but not "b," implies that NO_2 observed at the site originates from source category A rather than from category B.

In the case of NO_x emissions, carbon monoxide (CO) serves as a reliable indicator of NO_2 originating from mobile sources. In 1977, nearly all (i.e., 96 percent) of manmade NO_x was emitted from two source categories: mobile sources and stationary fuel combustion sources.[1] Ninety-nine (99) percent of the CO emanating from these two source categories came from mobile sources. Reference 1 also indicates that sulfur dioxide (SO_2) should serve as a useful indicator of NO_2 emanating from stationary combustion sources. In 1977, 97 percent of SO_2 from mobile or stationary source combustion sources originated from the latter. Hence, subject to some caveats which will be identified later, four results are possible:

1) Close correspondence between NO_x and CO but not with SO_2. Conclusion: mobile sources are responsible for observed NO_2 peaks.

2) Close correspondence between NO_x and SO_2 but not with CO. Conclusion: stationary combustion sources are responsible for observed NO_2 peaks.

3) Close correspondence between NO_x and both CO and SO_2. Conclusion: both mobile and stationary combustion sources contribute significantly to observed NO_2.

4) Lack of correspondence of NO_x with either CO or SO_2. Conclusion: a stationary source not characterized by SO_2 emissions (e.g., nitric acid plant, power plant burning natural gas) may be impacting the monitoring site.

Use of CO and SO_2 tracers in the analysis of ambient NO_2 data proceeds by plotting diurnal NO, NO_2, CO and SO_2 concentration patterns observed concurrently at a monitoring station. This procedure has been extensively followed using 1975-1977 SAROAD data to examine coincident NO, NO_2, CO and SO_2 peaks. Figure 7.1 exemplifies what was, by far, the most frequent finding -- close correspondence between diurnal CO and NO or NO_2 concentrations with little apparent correspondence with SO_2 concentration profiles. This finding is not too surprising when one considers that mobile source emissions of NO_x and CO are ubiquitous and occur near the ground. Most of the stationary source emissions of SO_2 and NO_x occur as the result of combustion by electric utilities or industrial sources.[1] Emissions from such sources are generally confined to restricted areas or "points" defined by the location of the emitting facility. Frequently, these point source emissions occur through elevated stacks. Hence, the likelihood of a plume from such a source impacting at the precise location(s) of a monitoring station(s) for a better part of an hour or more is slight.

Despite the fact that the impact of point sources of NO_x emissions is seldom detected by existing monitoring networks, monitoring data exist which demonstrate the potential for point sources to contribute to high hourly

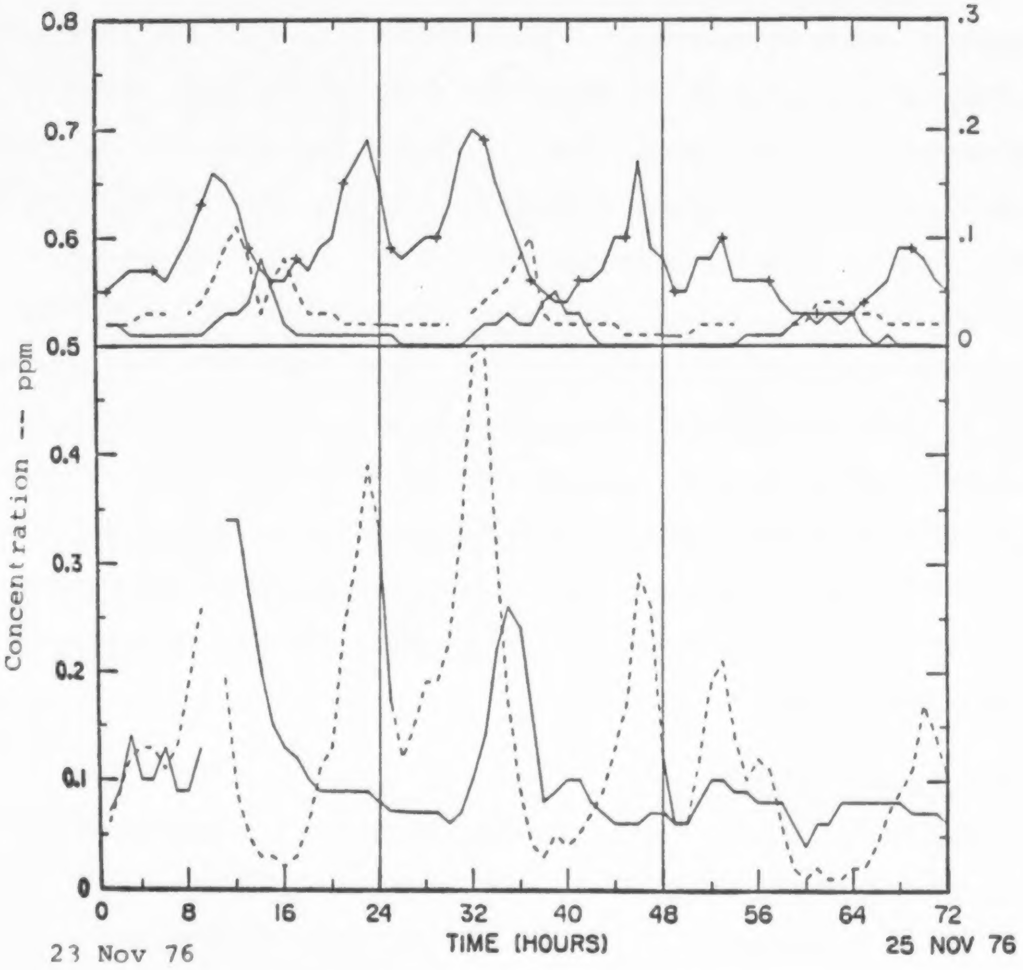


Figure 7.1 Pollutant plots for Lynwood, November 23-25, 1976.

Upper panel: O_3 (-----), CO (+—+—), and SO_2 (—); CO concentration scaled by 0.01
Lower panel: NO (-----), NO_2 (—)

concentrations of NO_2. In Figures 7.2 and 7.3, for example, SO_2 tracer data demonstrate that superposition of a point source plume on background NO_2 can result in NO_2 concentrations above 0.20 ppm in winter, as well as in summer.

Before leaving the subject of SO_2 and CO tracers, several caveats regarding the approach need to be identified. First it should be recalled that the approach identifies possible causes of high NO_2 at the monitoring site only. Source categories not having any apparent impact at existing monitoring sites are not necessarily unimportant. Second, there may be stationary sources of NO_x which do not emit SO_2 (e.g., nitric acid manufacturing, natural gas pumping stations or natural gas-fired utilities). These sources could impact on a monitoring site without being identified as stationary sources. Third, relatively small amounts of SO_2 and CO are emitted by stationary area sources of NO_x such as residential oil burners. Hence, SO_2 is not uniquely identified with large stationary point sources nor is CO uniquely identified with mobile sources. Finally, relative amounts of NO_x versus CO versus SO_2 emitted from sources within a given source category vary. For all these reasons, the approach outlined in this section can only be regarded as qualitative.

7.2 Use of Peak-to-Mean Ratios

Calculating the ratio of peak hourly NO_2 concentration to mean NO_2 concentration can sometimes be useful

(a) in determining whether point source impact is likely, and

(b) in assessing whether a short term or annual air quality goal is more restrictive.

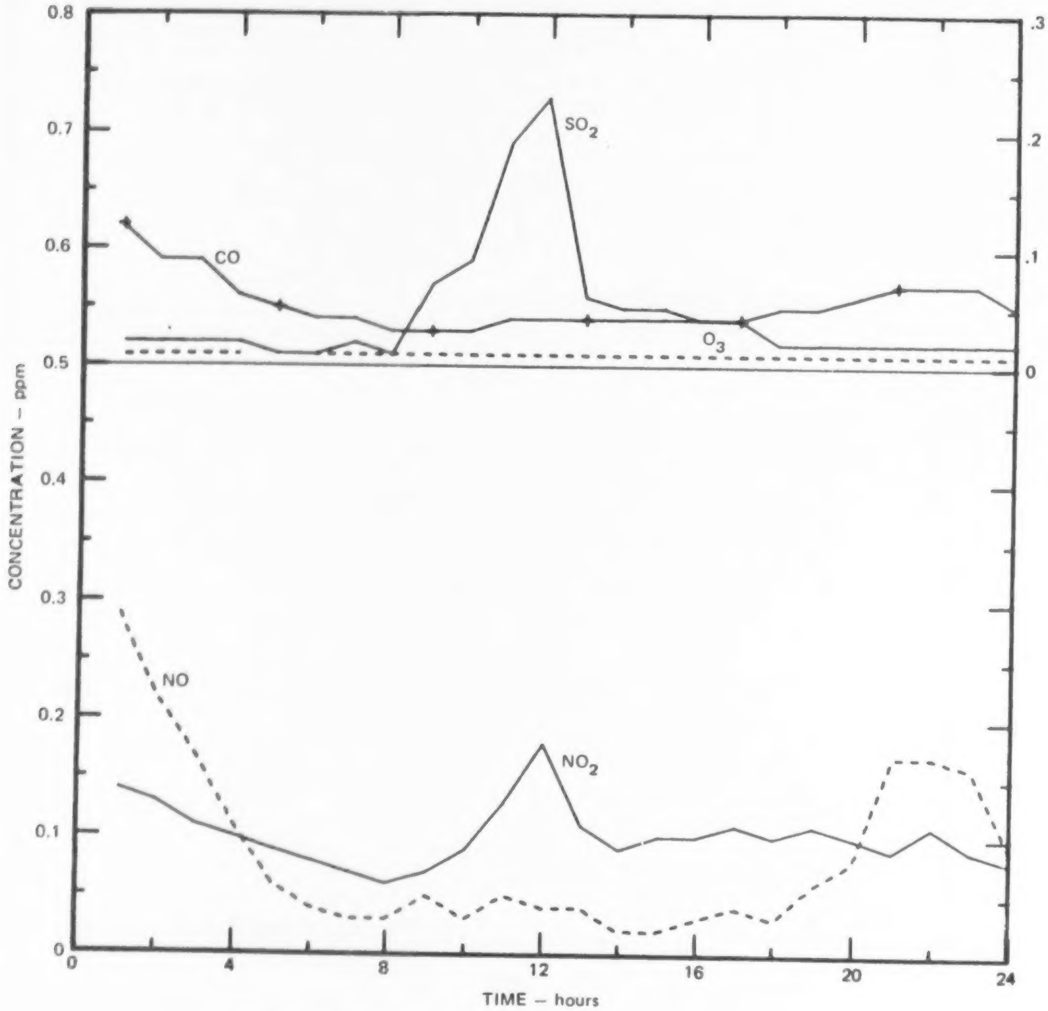


Figure 7.2 Example of potential point source impact at Long Beach on Sunday, 16 November 1975. CO has been scaled by 0.01.

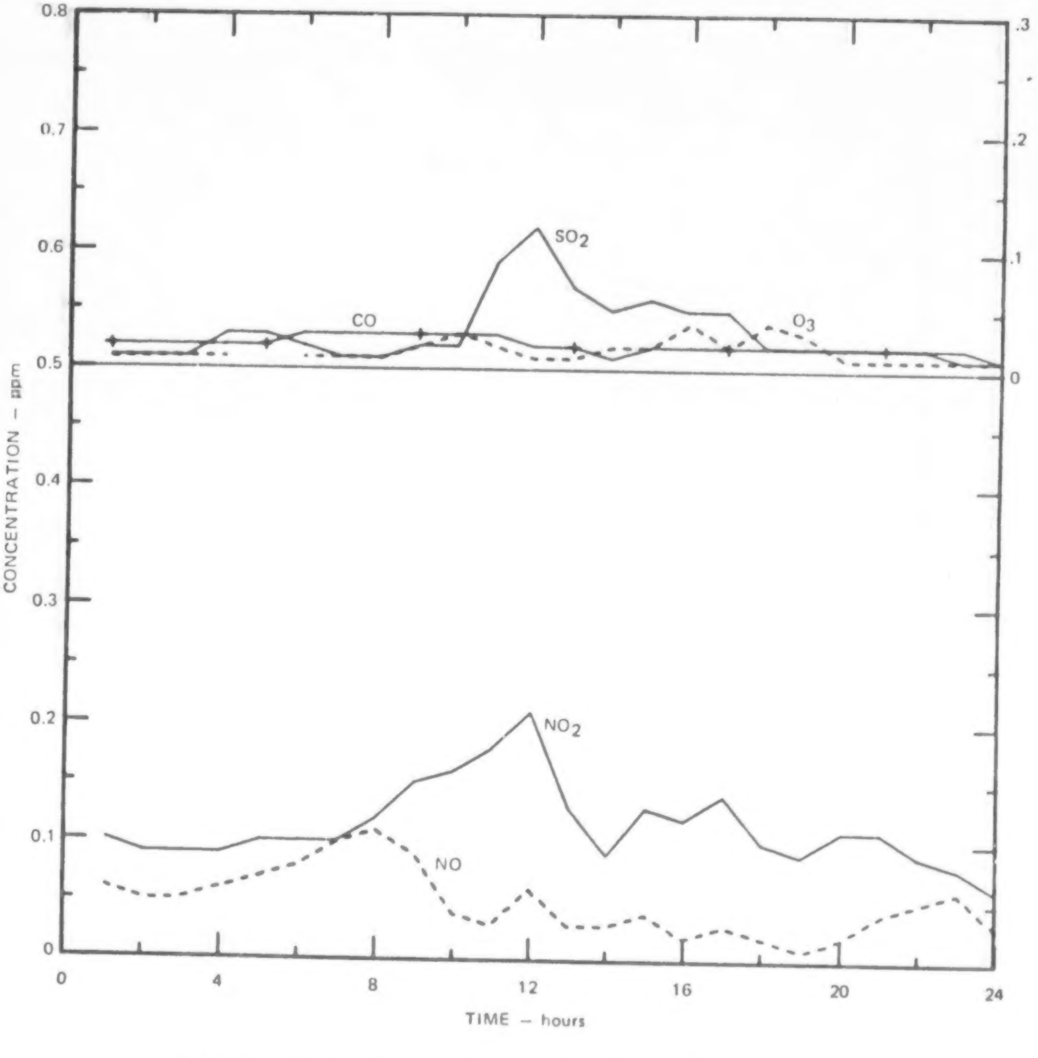


Figure 7.3 Example of potential point source impact at Whittier on Monday, 25 August 1975.

CO has been scaled by 0.01.

One would ordinarily expect that a monitoring station which was impacted by a large, elevated point source of NO_x would exhibit higher peak-to-mean ratios than a site which is impacted by ubiquitous area sources of NO_x. This assertion is based on the presumption that it is extremely unlikely that a plume from an elevated point source will impact at a given groundlevel station. Hence, the mean concentration will be low, but the peak concentration could be high, yielding a high peak-to-mean ratio. Conversely, there will always be some impact attributable to ubiquitous groundlevel sources, so that one would expect a lower peak-to-mean ratio when such sources dominate.

Peak-to-mean ratios may also be useful in assessing whether it will be more difficult to comply with an annual or hourly air quality goal for NO_2. This information may, in turn, be useful in the design of control strategies since the relative effectiveness of different strategies could be different for annual versus short term problems. To illustrate, suppose the short term air quality goal were 0.25 ppm NO_2 not expected to be exceeded more than once per year and the annual goal were 0.05 ppm. At sites having peak-to-mean ratios in excess of 5:1 (i.e., .25/.05=5), the short term air quality goal is likely to be of greatest concern.

As suggested in Section 7.1, an extensive review of NO_2 data has indicated that monitoring stations experiencing NO_2 concentrations in excess of 0.20 ppm are dominated by mobile (i.e., ubiquitous area) sources of NO_x.[9] Under such conditions, Martinez and Nitz found peak-to-mean NO_2 ratios varying between 3 and 12 with a median value of 6.3 and about 70 percent of the values between 5 and 7.6.[9] These findings are similar to ones found by Trijonis using earlier data from 120 urban sites throughout the United States.[21] Trijonis has also found a distinct difference between urban peak/mean ratios and ratios measured in rural areas subject to occasional impacts from elevated point sources. This difference is depicted in Figure 7.4. Figure 7.4 indicates that if the impact of area sources of NO_x (e.g., mobile sources) or ambient NO_2 is insignificant compared to that from elevated point sources, the peak-to-mean ratio is likely to be high. Unfortunately, the converse of this does not necessarily follow. That is, one cannot rule out the possibility of a point source significantly impacting at a monitoring site just because the peak-to-mean ratio is low. Thus, although fewer data are needed to apply the peak-to-mean ratio versus the tracer approach, the latter approach is more useful. The principal utility of the peak-to-mean ratio approach is to identify cases in which point source impacts occur and the impact of area sources is negligible.

7.3 Impact of Point Sources on Ambient Levels of NO_2

Information presented in Sections 7.1 and 7.2 implies that existing NO_2 monitoring sites tend to reflect the impact of area (mobile) sources. However, for an analysis of potentially harmful exposures to NO_2, it is necessary to consider the impact on ambient NO_2 of large point sources as well. Air quality data collected in the vicinity of large point sources give insight into how such sources should be considered in models to estimate needed controls. In this section, information collected at a continuously operated groundlevel monitoring network in the vicinity of the Clinch River (TN) power plant is described. Next, evidence of point source plumes observed during the St. Louis RAPS study is described. Third, air quality measurements taken within the plumes of several large point sources using instrumented aircraft are discussed. Finally, implications about appropriate methods for modeling such sources are identified.

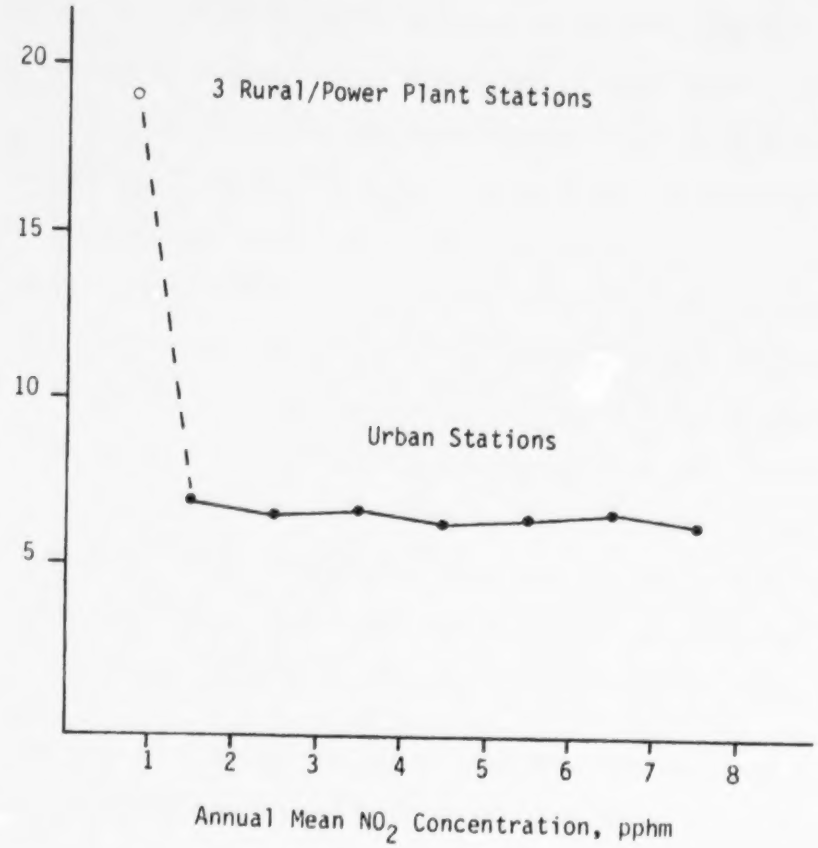
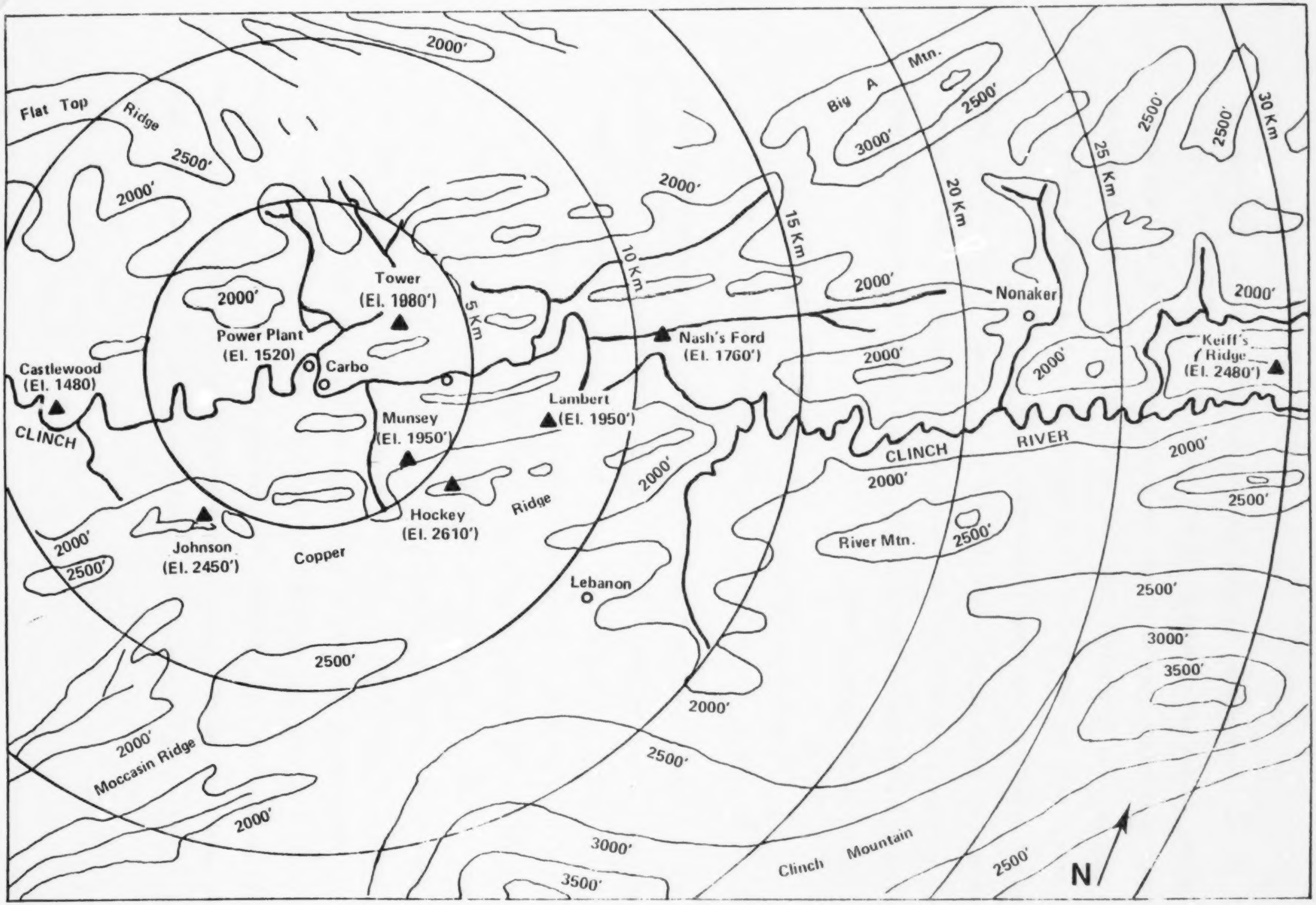


Figure 7.4. Dependence of maximum/mean ratio on annual mean NO_2 concentrations.

The Clinch River power plant is a 712 MW coal fired utility located in complex terrain. NO, NO_x and SO_2 monitoring data were collected for approximately 1-1/2 years at six continuously operated monitoring stations shown in Figure 7.5. For reference in Figure 7.5, the top of the plant's stack is located approximately 2,175 feet above sea level. Several observations are apparent.

1. The most striking observation is the infrequency with which the network detected a major impact attributable to the source. Of approximately 120,000 station-hours of observations, hourly NO_x values in excess of 0.20 ppm were observed only 59 times or about 0.05 percent of the time. The highest hourly reading was 0.83 ppm NO_x. Only three NO_2 concentrations in excess of 0.20 ppm were recorded (0.0025 percent of the time). These three readings range from 0.35 - 0.74 ppm and are suspicious in that the corresponding NO_x data are either missing or agree closely with the recorded NO_2 value. It should be pointed out, however, that observed instances of NO_2 in excess of 0.20 ppm would likely have been more frequent in an area subject to high concentrations of ozone. Although the data are not available, it is unlikely that Clinch River experiences hourly ozone concentrations in excess of 0.10 - 0.15 ppm.

2. Approximately 50 percent of the NO_x values in excess of 0.20 ppm occurred between 9 a.m. - 12 noon, giving credence to the hypothesis that the maximum impact from such sources is likely to be during the period in which morning fumigation occurs. Twenty-five (25) percent of the time high NO_x was observed between 6 p.m. and 9 a.m. This is surprising, but it could reflect the presence of katabatic winds. Such a finding is not likely in flat terrain.


Flat Top Ridge
2500'
2000'
Power Plant
(El. 1520)
Carbo
Tower
(El. 1980')
5 Km
10 Km
15 Km
20 Km
25 Km
30 Km
Castlewood
(El. 1480)
CLINCH
Munsey
(El. 1950')
Hockey
(El. 2610')
Johnson
(El. 2450')
Copper
Ridge
Lambert
(El. 1950')
Nash's Ford
(El. 1760')
Lebanon
Nonaker
Keiff's Ridge
(El. 2480')
Big A Mtn.
3000'
CLINCH RIVER
River Mtn.
Moccasin Ridge
Clinch Mountain
3500'
N

Stack Height ~ 200 m

Figure 7.5 Location and Elevation of Clinch River Power Plant Stations.

3. During hours in which observed NO_x was $\geq$ 0.20 ppm, 90 percent of the NO_2/NO_x ratios varied between .10 and .50, as shown in Figure 7.6. There is a slight negative correlation between the NO_2/NO_x ratio and NO_x on these days with high NO_x. It is possible that observed NO_2/NO_x ratios during periods with high ground level NO_x attributable to a point source may be somewhat higher in locations subject to high ozone concentrations. As in Figure 7.7 suggests, the median NO_2/NO_x ratio observed in this sample is about 0.25. The three occasions in which hourly NO_2 concentrations in excess of 0.20 ppm were observed are all characterized by NO_2/NO_x ratios which lie far outside the range observed on every other occasion.

4. As expected, there was an excellent correspondence between hours with high NO_x and hours with high SO_2 observed by the Clinch River network.

In addition to the Clinch River data, air quality data were measured aloft on 134 days during the RAPS study in St. Louis. A subset of these data have been reduced by Evans.[24] These data are of particular interest, because they were observed in an urban area. Evans' data frequently reveal evidence of NO_x plumes aloft. In a few cases, such as the one illustrated in Figure 7.8, very high (> 1.0 ppm) NO_x concentrations were observed for periods of a minute or two. However, in such cases the plume consisted almost entirely of NO. The amount of NO_2 present in such plumes is consistent with the depletion in the ambient ozone levels found within the plume as a result of the titration reaction. It is also of interest to note that despite the presence of these plumes aloft, only six daily maximum hourly NO_2 readings were observed above 0.20 ppm by the 25 station RAPS network during 1976. Five of these readings occurred between 8:00 p.m. and midnight LCT. The sixth reading occurred at 9:00 a.m. Five of the high values

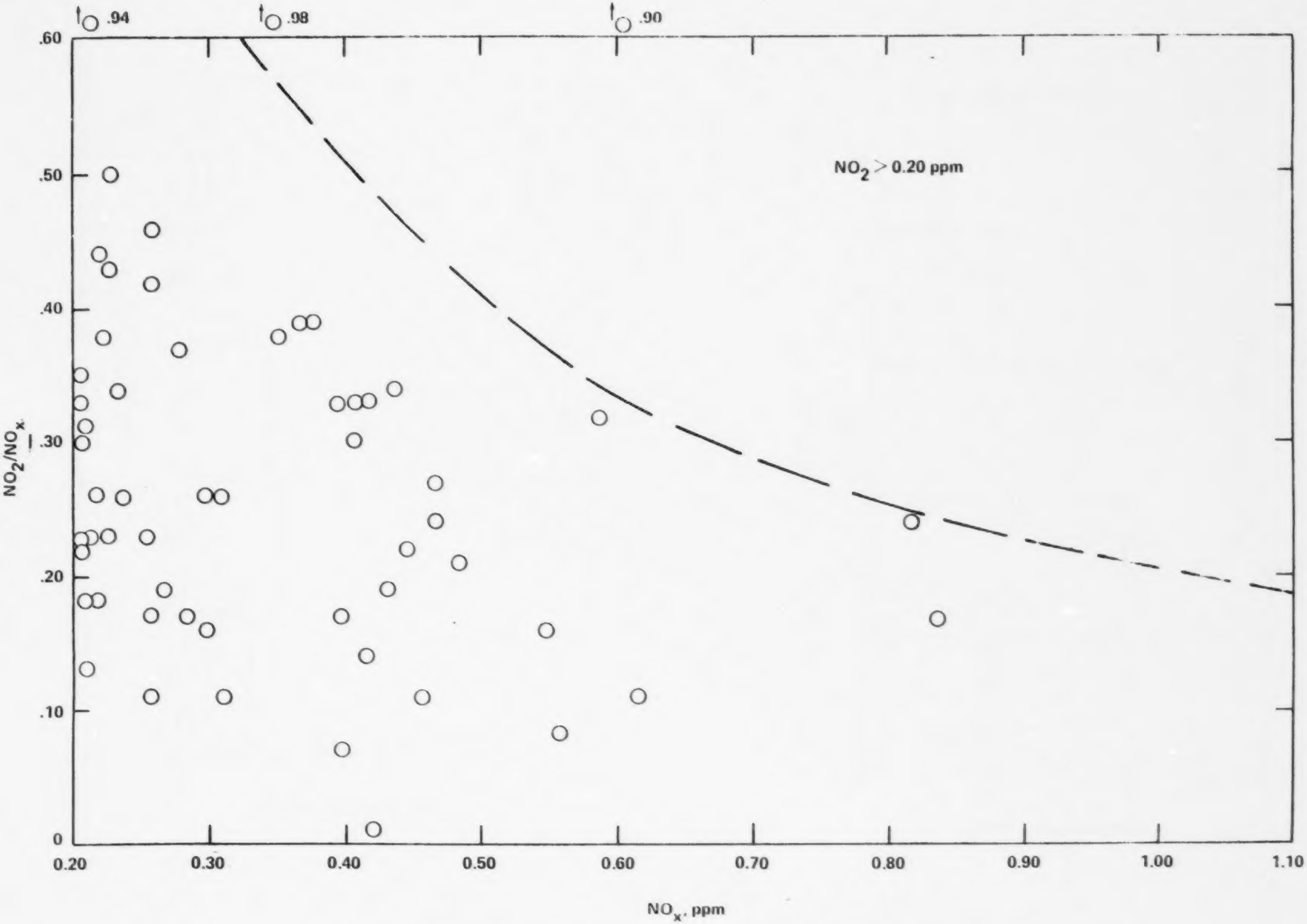


Figure 7.6 NO$_2$/NO$_x$ vs. NO$_x$ at Clinch River on Days with High NO$_x$.

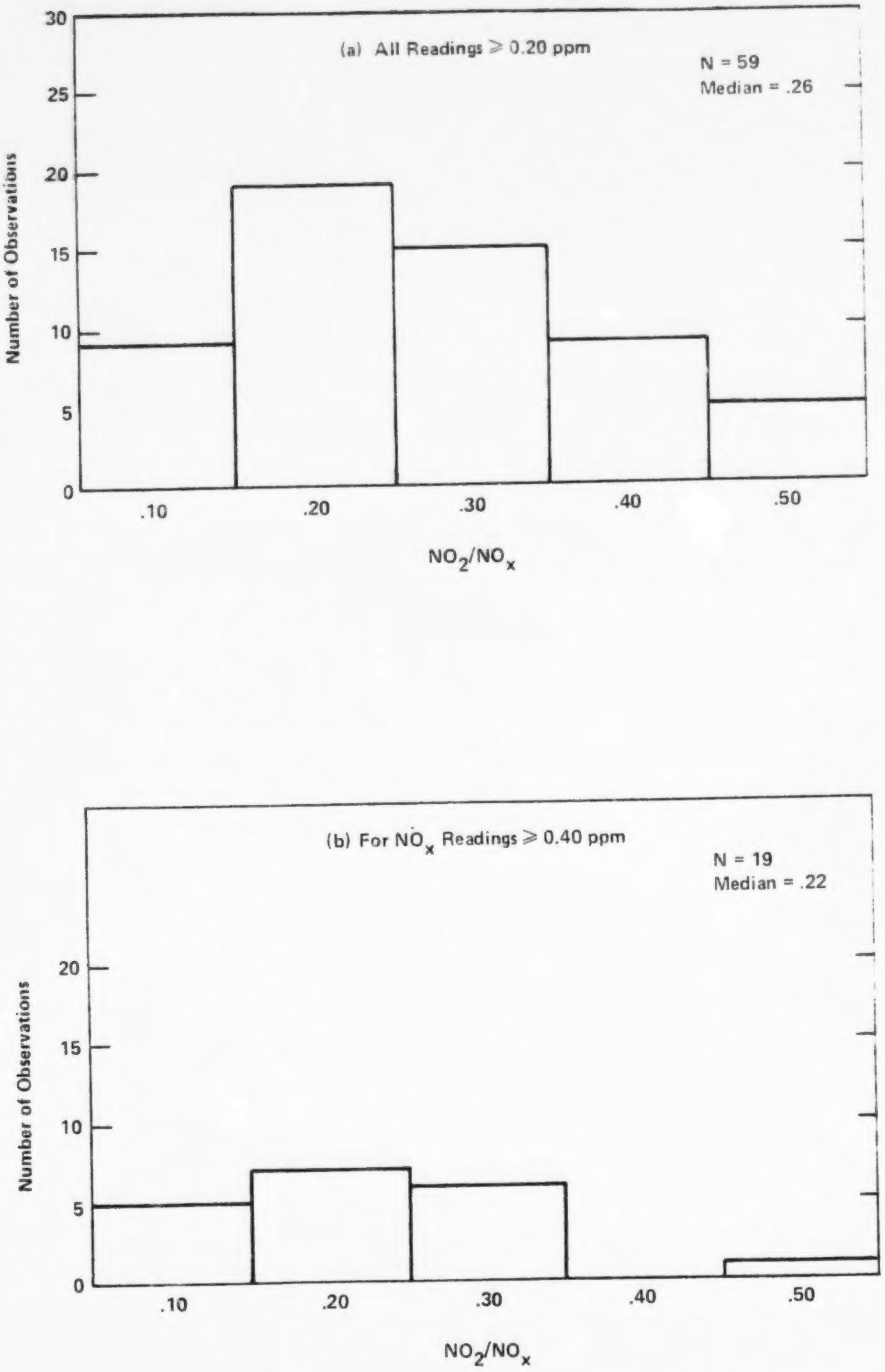
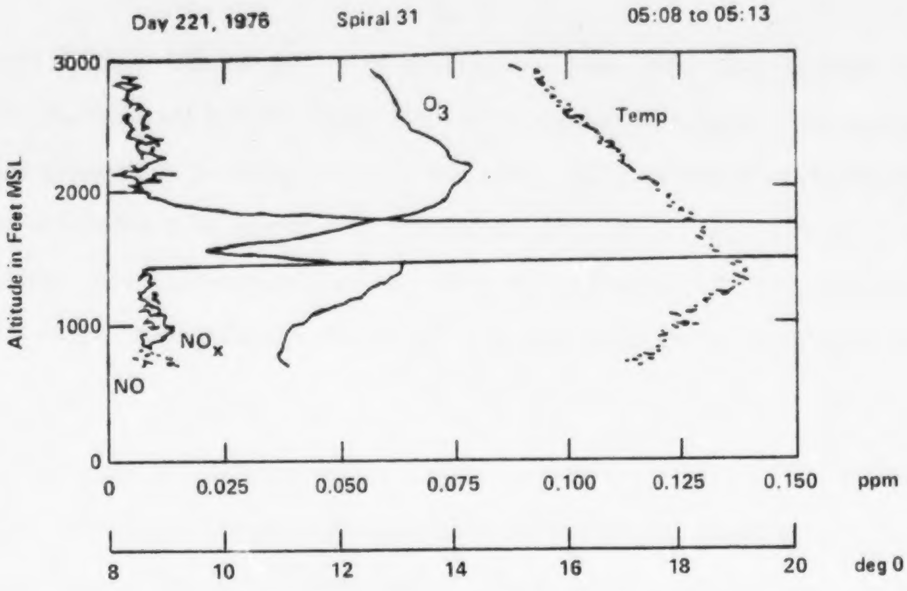
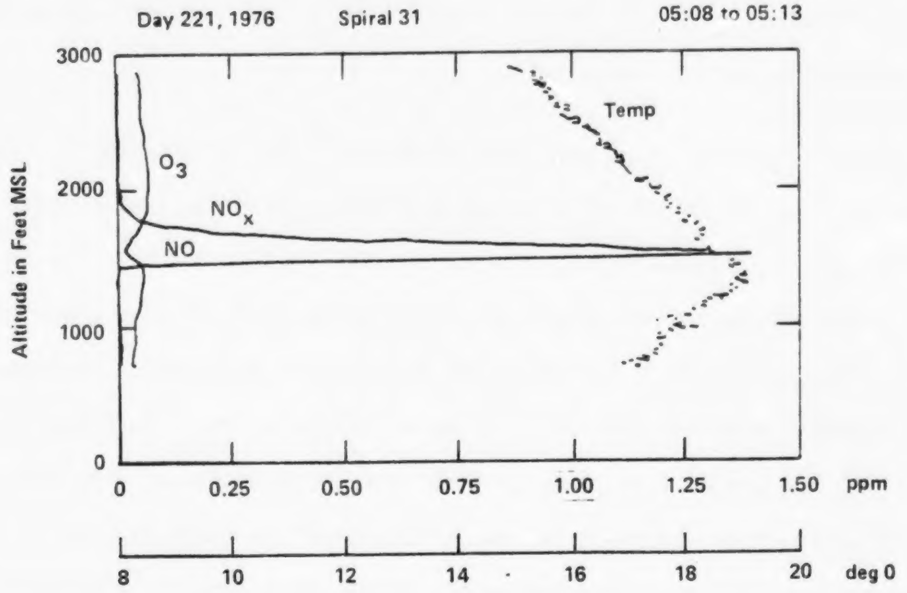


Figure 7.7 NO_2 Ratios Observed at Clinch River During Hours with High Ambient NO_x.



Ozone, NO, NO_x, and Temperature vs. Altitude, Day 221



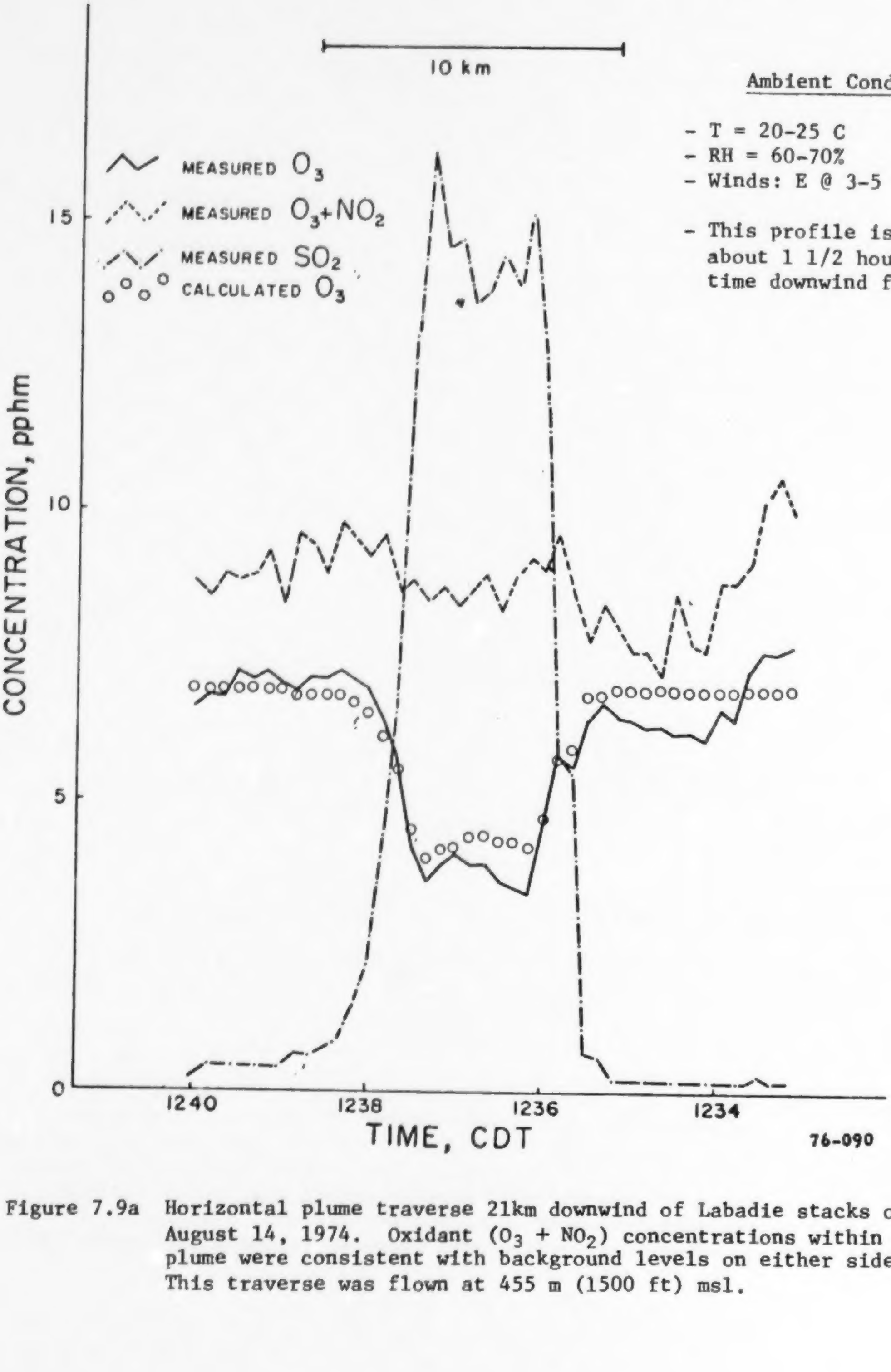
Ozone, NO, NO_x, and Temperature vs. Altitude, Day 221

Figure 7.8 Evidence of NO_x Aloft Over St. Louis.

occurred on October 1-2, 1976, days with atmospheric stagnation in which several sites observed above-normal readings. The sixth high reading occurred at 10:00 p.m. on a Friday night in November 1976. Only one site recorded an abnormally high reading on this occasion. This tends to support the theory of a point source impact. However, the time at which the high reading occurred (10 p.m.) makes it seem more likely that the data reflect the impact of a local ground level source or are spurious.

The final set of data which sheds insight on the behavior of point source plumes of NO_x is obtained from aircraft measurements made within plumes. Studies of this nature are generally conducted by flying traverses at various distances downwind from the source. By noting cross sectional variations in NO_2, NO, O_3 and SO_2, at differing distances (travel times), the validity of various plume modeling approaches can be checked.

Airborne measurements have been made of several power plant plumes. Perhaps the most extensively reported set of measurements has been those made within the plume of the Labadie power plant as part of the MISTT project.[25,26] The Labadie source is a 2200 MW coal-fired power plant located about 50 km WSW of downtown St. Louis. Figures 7.9 and 7.10 show cross sectional concentration patterns 21 and 45 km downwind from the Labadie plant on a particular day. In Figures 7.9a and 7.10a, SO_2 measurements are used to trace the cross sectional dimension of the power plant's plume. Because the "O_3 + NO_2 curve" in these figures is constant, it is apparent that the net formation of NO_2 within the plume is practically identical to the net loss of ozone within the plume. This strongly implies that NO_2 formation within the plume occurs as the result of the titration reaction (i.e., reaction 3.1). White et al.[25,26] have shown that a simple model which



Ambient Conditions

- T = 20-25 C
- RH = 60-70%
- Winds: E @ 3-5 m/sec
- This profile is measured about 1 1/2 hours travel time downwind from source.

Figure 7.9a Horizontal plume traverse 21km downwind of Labadie stacks on August 14, 1974. Oxidant (O_3 + NO_2) concentrations within plume were consistent with background levels on either side. This traverse was flown at 455 m (1500 ft) msl.

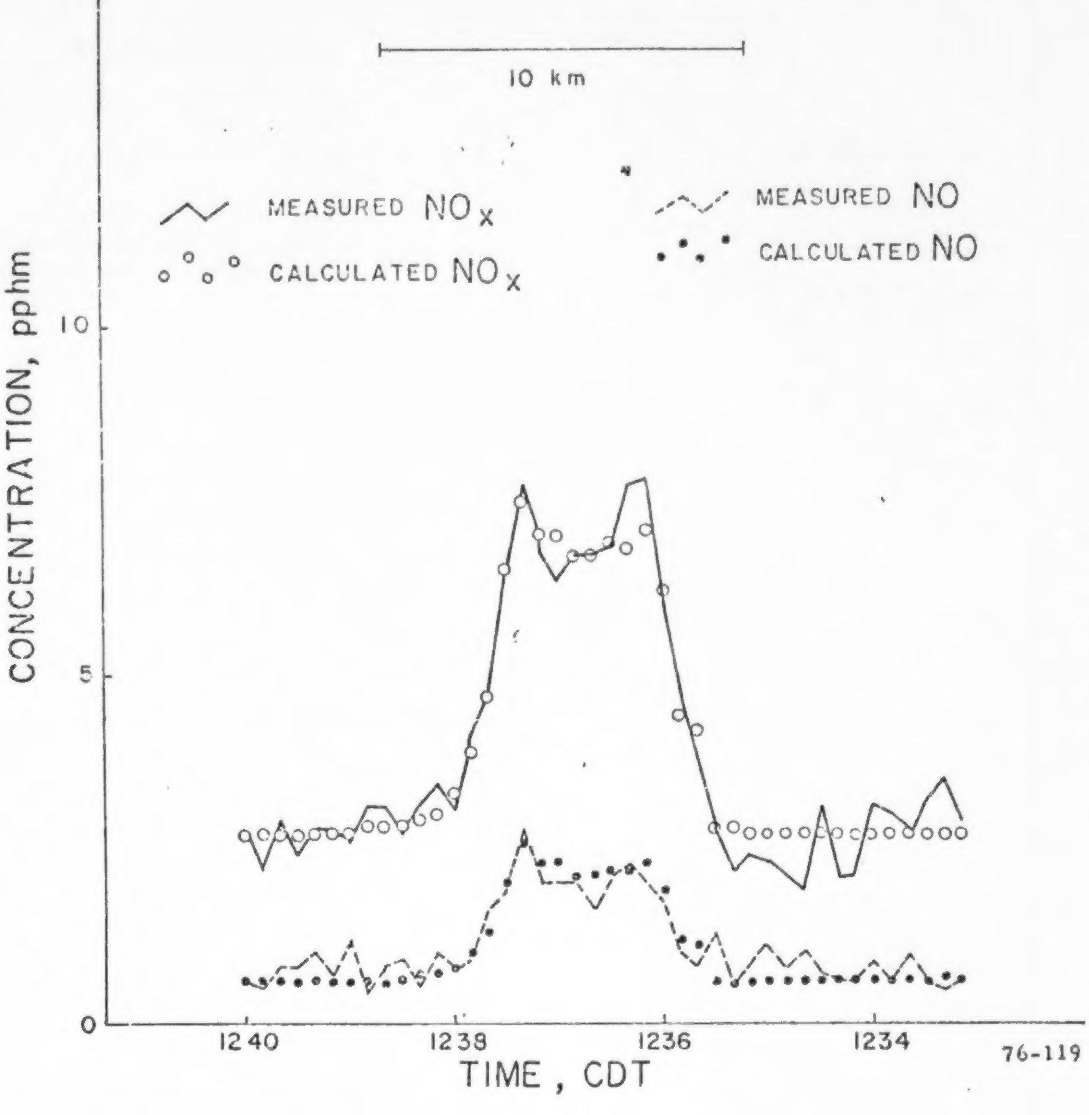


Figure 7.9b Horizontal plume traverse 21km downwind of Labadie stacks on August 14, 1974. Most of the NO emitted by the power plant had already been oxidized to NO_2. Measured NO_x profile agreed well with NO_x profile scaled from measured SO_2 concentrations. Measured NO profile agreed well with No profile calculated from measured SO_2 profile and oxidant-preserving photochemistry. (The same traverse is shown in Figure 7.9a).

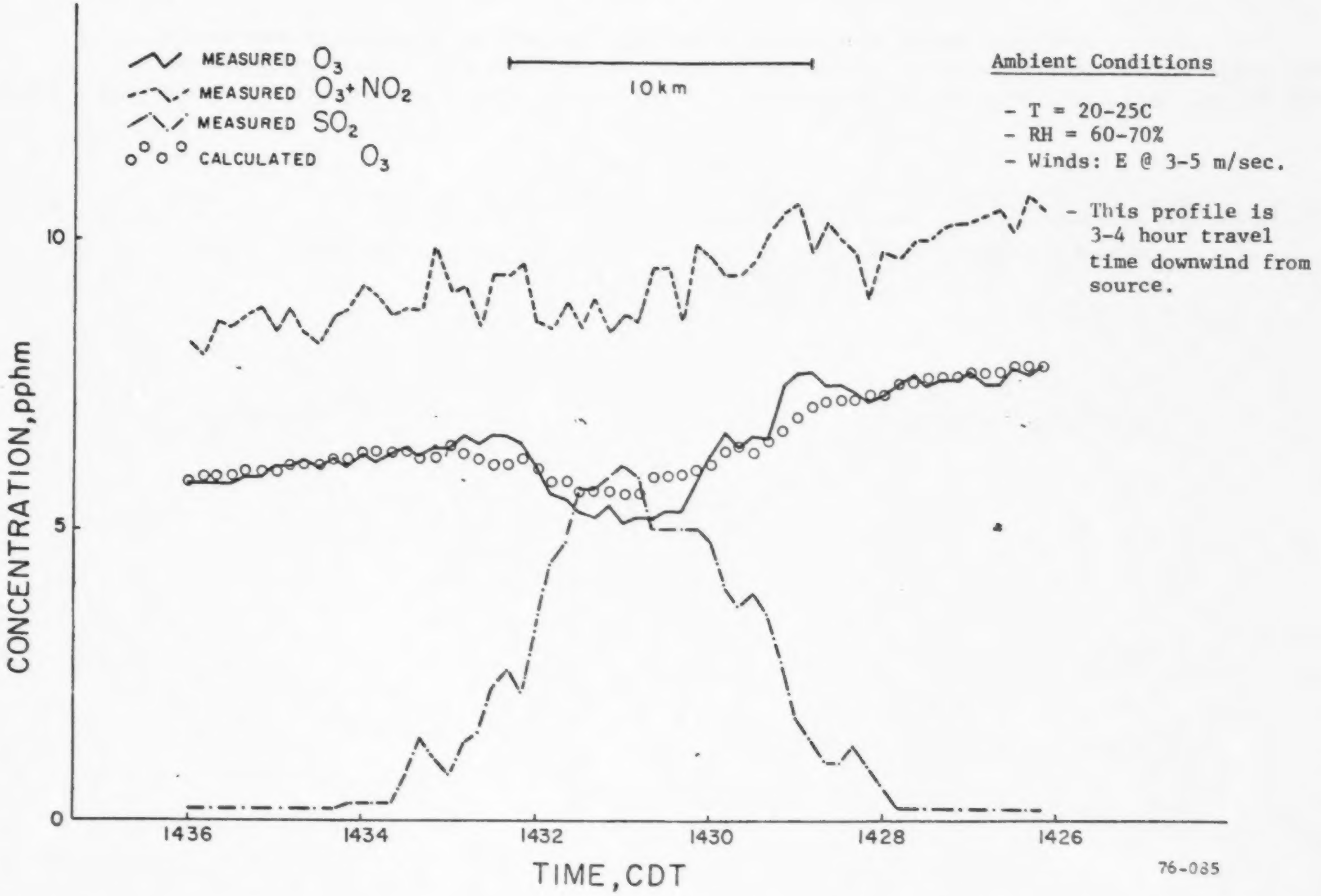


Figure 7.10a Horizontal plume traverse 45 km downwind of Labadie stacks on 14 August 1974. Ozone concentrations within the plume at this distance were still depressed below background levels on either side, although not as strongly as on traverses nearer the stacks. Measured ozone and oxidant profiles both show large-scale concentration gradient, possible due to urban plume from Greater St. Louis. The altitude of this traverse was 610 m (2000 ft) msl.

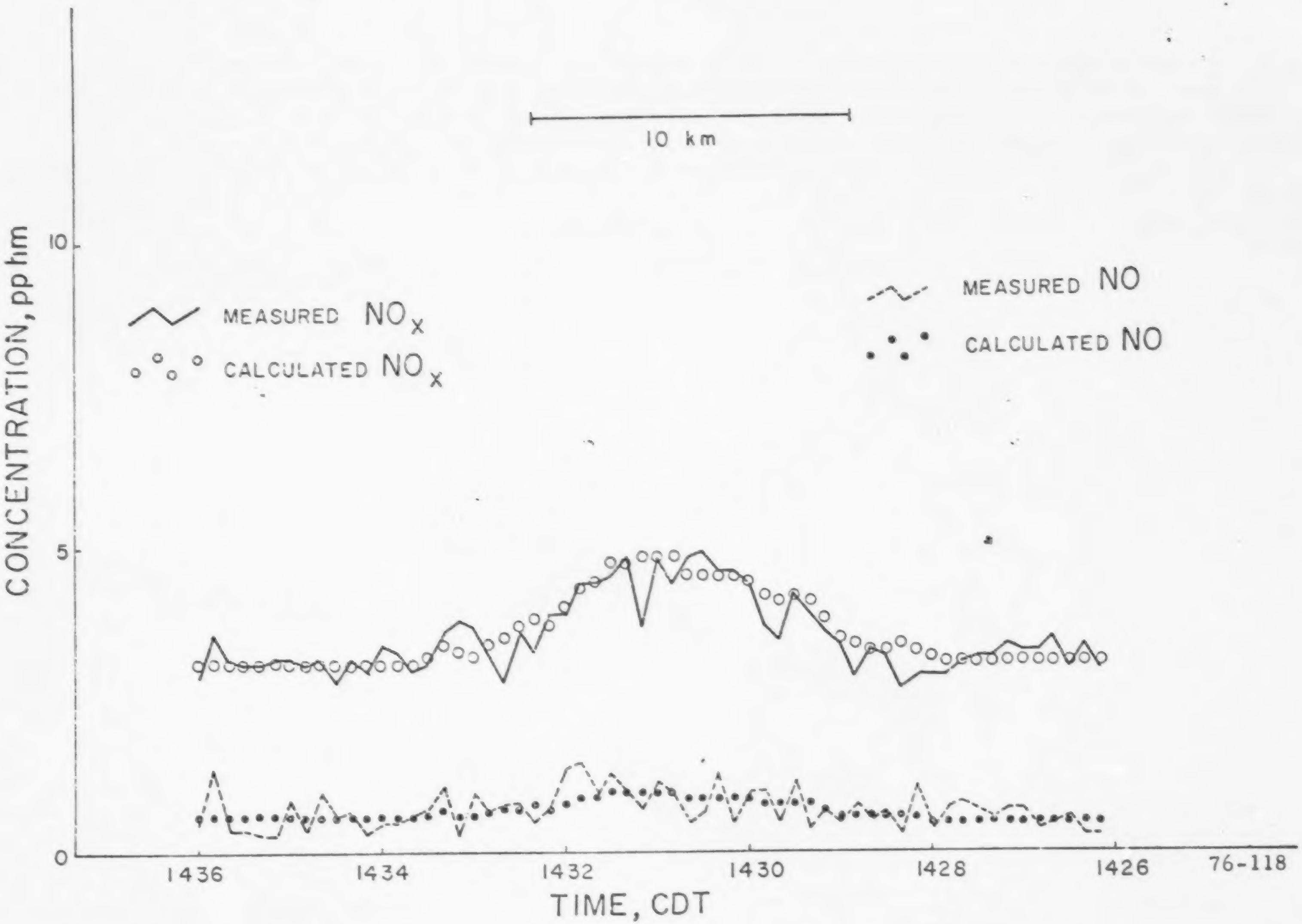


Figure 7.10b Horizontal plume traverse 45 km downwind of Labadie stacks on 14 August 1974. Nitric oxide concentrations were near the detection limit of the monitor, and very little excess within the plume was observed or predicted. (The same traverse is shown in Figure 7.10a.)

assumes that NO_2, NO and ozone concentrations within the Labadie plume can be estimated using an empirical relationship between SO_2 and NO_x and the photostationary state* assumptions.[26] As shown in Figures 7.9 and 7.10, excellent agreement between the model and observations is obtained. On the basis of these results, White concludes that, within 40 km of the source, NO_2 and O_3 concentrations within the plume are not affected by reactions with organic pollutants.

Hegg _et al_. have summarized findings from monitoring studies within the plumes of two coal-fired utilities and two gas-fired plants.[27] These observations are essentially similar to those found in the Labadie plume. Hegg _et al_. conclude that the conversion of NO to NO_2 within a power plant plume is limited by the rate with which this NO comes into contact with ambient ozone. In short, conversion of NO to NO_2 is limited by the dilution rate. These results can be interpreted to mean that the fraction of NO_x which is NO_2 (i.e., NO_2/NO_x) will be greater near the periphery of a plume than at the centerline. Figure 7.11 illustrates this concept. Hence, peak NO_2 concentrations may not occur in the same position in the plume as peak NO_x concentrations (i.e., at the centerline). Locations within the plume experiencing high NO_x have, necessarily, been exposed to relatively little dilution air. Exposure to dilution air is necessary for conversion

---

* The Photostationary State assumes that an equilibrium between the reactions

$$O_3 + NO \xrightarrow[k_2]{} O_2 + NO_2 \qquad \text{(i.e., the titration reaction)}$$

and

$$NO_2 + O_2 \xrightarrow[k_1]{h\nu} O_3 + NO \qquad \text{(reaction of resulting } NO_2 \text{ with sunlight)}$$

occurs. This equilibrium is given by

$$\frac{k_1}{k_2} = \frac{[O_3]\,[NO]}{[NO_2]}$$

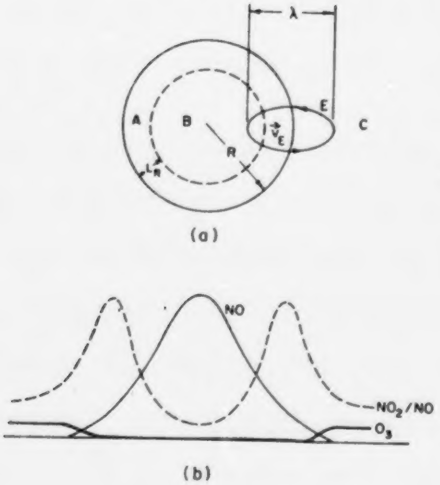


Figure 7.11 Diagrams for a titration reaction in a turbulent plume: (a) shows a cross-sectional view of the plume. The reaction zone is an annulus of Area A and width L_R. The interior of the plume, where the concentration of NO is high, has area B. Area C is the exterior region of ozone. E is a mixing turbulent eddy of velocity V_E and scale λ: (b) shows concentrations of the gases across section (a).

Source: Reference 27

of NO to NO_2 to proceed. However, dilution reduces NO_x concentrations. Thus, there are two counteracting phenomena (dilution and chemical conversion) which should theoretically limit peak NO_2 concentrations within the plume of a major point source. A result of these competing phenomena is that NO_2/NO_x ratios are likely to be higher at the plume's periphery than at the centerline. This is illustrated in Figure 7.11. Maximum NO_2 concentrations are most likely at intermediate ranges where sufficient dispersion has occurred to bring the plume to the surface and to bring the reactants together. Further downwind dilution will diminish concentrations.

Before ending the discussion of NO_x point source plumes, one further point needs to be addressed. When concentrations of NO are very high (as they would be within a few hundred meters of a source), Reaction (7.1) may result in some initial conversion of NO to NO_2 without substantial dilution.

$$2\ NO + O_2 \rightarrow 2\ NO_2 \qquad (7.1)$$

The rate with which Reaction (7.1) proceeds is too slow for it to be significant unless NO concentrations are very high.[2] As a result of Reaction (7.1) and direct emissions of NO_2, approximately 5-10 percent of "initial" NO_x from combustion sources will be usually be NO_2. NO_2/NO_x ratios can, however, be as high 0.25 as the result of the reaction (7.1).[2] Hence, it is possible to have high NO_2 concentrations at the plume centerline without substantial dilution. However, the extent to which such an undiluted plume impacts the ground is probably very limited.

7.4 Implications

1. Use of SO_2 and CO data as tracers is a useful qualitative approach for assessing whether observed high NO_2 concentrations are primarily attributable to

stationary or mobile sources. Estimating peak-to-mean ratios of NO_2 serve as a useful approach (a) for verifying whether a major point source is impacting a site sporadically, and (b) for assessing whether a short term or annual air quality goal for NO_2 is going to be more difficult to meet at a given site. Such tools provide qualitative insights (a) on whether to emphasize control strategies impacting most heavily on ubiquitous area sources or on large point sources, and (b) on whether to stress control strategies which emphasize reducing short term peaks or long term averages.

2. Application of tracer data and peak to mean ratios to available NO_2 data suggest that observed NO_2 concentrations in excess of 0.20 ppm are usually attributable to mobile sources. This finding could, in part, reflect a bias in the way existing monitors are sited (i.e., frequently near roadways). However, the data examined indicate that, even when a monitoring network is deployed so as to maximize the likelihood of detecting the impact of an elevated point source, observed high hourly concentrations of NO_x (and NO_2) resulting from such a source are very infrequent. The foregoing implies that strategies which stress reduction of NO_x emissions from mobile and area sources will be most effective in reducing observed short term peak NO_2 concentrations as well as annual average values. Nevertheless, as a safeguard, when possible a case-by-case review of tracer data is suggested.

3. The preceding paragraph should not be interpreted to mean that major point sources of NO_x necessarily play an insignificant role in the NO_2/ozone problem. Paragraph 2 referred solely to observed data collected at continuously operated ground level monitors. Such networks are usually quite sparse. Aircraft data reveal occasional very high (e.g., > 1.0 ppm) concentrations of NO_x as

well as moderate concentrations of NO_2 within point source plumes. These NO_2 concentrations, when superimposed upon the NO_2 resulting from other sources could lead to hourly concentrations in excess of concentrations as high as 0.20 or 0.25 ppm. Because (a) NO_x emitted within point source plumes (without substantial amounts of VOC) may be less photochemically active than NO_x from well-mixed sources, and (b) NO_x from elevated sources may be more isolated from the ground and other scavengers, NO_x from such sources may be relatively more important in the transport of low levels of NO_x to rural areas. As such, they could be potentially more important in the formation of ozone in rural areas, formation of fine particulates over great distances, and as a contributing factor in the acid deposition phenomenon.

4. Data collected within point source plumes suggest that NO_2 within such plumes primarily results from titration of NO with ambient ozone. Some NO_x may be emitted as NO_2 as well. Because of the high concentrations of NO_x which may occur within plumes, the ozone titration reaction is likely to be limited by the concentration of ambient ozone. This suggests that the most effective way of reducing peak NO_2 from a point source may be (a) to limit the amount of NO_x emitted as NO_2 or converted to NO_2 via the oxidation reaction described in Reaction (7.1). and/or (b) reduce ambient levels of ozone as the result of SIP's for ozone. However, reduction of NO_x emissions in any form may be useful in reducing ozone formation in downwwind areas. Procedures for reducing NO_x from large stationary sources are described in the appropriate Control Techniques Document.[28]

5. To the extent that St. Louis is a typical city, data examined there suggest that plumes of NO_x are frequently present aloft in the early morning hours. Data from Clinch River tend to confirm that the midmorning fumigation phenomenon is the event most likely to lead to observed major impacts from elevated point sources. Hence, midmorning may be the most likely time to observe a major impact from point sources. Even with the fairly dense monitoring network in the RAPS study and the ideally sited network at Clinch River however, impacts on ambient NO_2 in excess of 0.20 ppm resulting from the fumigation phenomenon were seldom, if ever, observed.

8.0 USE OF MODELS FOR NO_2

Previous chapters have discussed sources of NO_x, means by which it gets converted to NO_2 in the atmosphere, issues relating to measuring representative values of NO_2, prevailing levels of NO_2 observed by existing monitoring networks, long range transport of NO_2, and relationships between NO_2, its precursors and principal source categories. This information is needed in order to make informed judgments about collecting and interpreting appropriate data for developing control strategies to reduce unacceptably high levels of ambient NO_2. Questions that still remain however are:

(1) "how much control is needed to meet an air quality goal for NO_2?" and

(2) "what is the impact of an individual source?"

The answers to such questions require quantitative estimates. The role of models is to provide means for making such estimates.

The purpose of Chapter 8.0 is to describe models available for estimating the impact of precursor emissions on short term and long term NO_2 concentrations. The state-of-the-art for NO_2 modeling is not so far advanced as for other criteria pollutants. Although some of the approaches to be described are easy to apply, such applications cannot be made blindly. Model assumptions or estimates which appear to contradict existing air quality, meteorological or emissions data need to be scrutinized and explained if they are to remain credible. The quantitative predictions provided by models should be regarded as "best estimates" with some band of uncertainty about them. Unfortunately, in most models for NO_2, this band of uncertainty is not precisely known. Such uncertainty is reduced, however, when use of models is accompanied by high quality input data, and is consistent with qualitative observations described in previous chapters. Under these conditions, model estimates provide useful quantitative goals for control programs.

The potential for high short term concentration of NO_2 is greatest in the following settings: (1) urban-industrial regions in which NO_x and VOC are emitted from a large number of mobile and stationary sources; (2) downwind of sources with large NO_x emission rates in urban regions or in non-urban regions which periodically experience high ozone levels (e.g., greater than the NAAQS for O_3); and (3) downwind of certain industrial sources that emit large quantities of NO_2 directly into the atmosphere. Accordingly, Sections 8.1 and 8.2 present models available for estimating the impact of controls in multisource urban areas and from large individual sources of NO_x or NO_2, respectively.

8.1 Multisource Urban Models

Models appropriate for use in multisource urban areas can be categorized as simple or complex. Simple models include linear rollback, OZIPM and the Photochemical Box Model (PBM). However, the only one of these approaches widely available as of September 1980 is rollback. Consequently, a more lengthy description of rollback modeling, as applied in assessing the impact controls on ambient NO_2 is provided herein. Complex models include several atmospheric simulation models. Such models have been primarily used to estimate ambient ozone concentrations, but can also produce estimates of ambient NO_2.

8.1.1 Linear Rollback

Linear rollback is based on the assumption that changes in emissions of a pollutant will result in proportional changes in the ambient concentration of that pollutant. It was concluded in Chapter 5.0 that background concentrations (be they natural or manmade) transported into the city under review may ordinarily be ignored. This simplifies the rollback model still further. The rollback approach proceeds by first estimating the future design value for NO_2 which would occur if no additional controls over and above those already planned were implemented.

$$\chi_f = (\chi_\circ) \left[\frac{Q_{future}}{Q_{present}} \right] \qquad (8.1)$$

where

χ_f = future NO_2 concentrations, any units

$\chi_\circ$ = present design value for NO_2, consistent units

Q_{future} = projected NO_x emissions, any units

$Q_{present}$ = present NO_x emissions, consistent units

The amount of additional reduction required in NO_x emissions to meet either the annual or a prospective short term NO_2 is given by Equation (8.2)

$$R = \frac{\chi_f - \chi^1}{\chi_f} \times 100 \qquad (8.2)$$

where

R = percent reduction required emissions over and above that already projected

χ^1 = the appropriate NAAQS for NO_2, consistent units.

Considerable efforts have been made to refine the "Q" terms on the right hand side of Equation (8.1) in recent years. These emission terms have been subdivided into different emission categories (e.g., light-duty motor vehicles, stationary combustion sources, etc.), each of which can reflect different assumptions about growth and future control technology.[29,30] As a result of these refinements, the model has come to be known as the "modified rollback" model. This model has been widely used in conducting regulatory analyses for prospective NO_2 air quality standards and for estimating the impact of various automotive emission standards on future NO_x emissions. The modified rollback model computer package and accompanying User's Manual will be available by 1981.

Several underlying assumptions in the linear rollback model need to be identified.

1) Peak and mean NO_2 concentrations are directly proportional to NO_x emissions;

2) Peak and mean NO_2 concentrations are independent of ambient NMOC (or VOC emissions);

3) Either all source categories are evenly distributed throughout the city or the atmosphere is perfectly mixed so that the relative contribution a source makes to ambient concentrations is the same as its relative contribution to total NO_x emissions.

As discussed in Chapter 6.0, the first assumption is generally valid for both peak and mean concentrations of NO_2. The exception occurs when peak NO_2 concentrations result primarily from titration of NO with ozone and the amount of NO_2 formed is limited by the prevailing O_3 concentration. Even in such a case, however, it is probably appropriate to assume that NO_2 is proportional to NO_x emissions, if the NO_2 peak is observed to build upon carryover NO_2. Thus, prior to applying the rollback model, it is advisable to apply the procedures described in Sections 3.2 and 3.3 to assure oneself that the observed peak NO_2 concentration is not limited by available ozone or that if it is, some carryover NO_2 is present.

According to the information presented in Chapter 6.0, average NO_2 concentrations are insensitive to changes in NMOC. Hence, the second assumption causes no problem in considering annual mean NO_2 values. However, peak NO_2 concentrations are slightly sensitive to reductions in NMOC. This sensitivity depends on the prevailing ambient $NMOC/NO_x$ ratio, diurnal emissions patterns and atmospheric dilution. Depending on these factors, reductions in peak NO_2 ranging from 0-20 percent have been observed to accompany 50 percent reductions of NMOC in smog chambers or in chemical kinetics models. It is not possible to consider relationships between peak NO_2 and NO_x and NMOC simultaneously using the rollback approach. However, NO_2 isopleth diagrams similar to those presented in Figures 6.5-6.7 have been used for several dilution rates and emission patterns to assess sensitivity of peak NO_2 to NMOC at various $NMOC/NO_x$ ratios. Table 8.1 presents the results obtained for low dilution rates most likely to accompany high urban levels of NO_x and NO_2. Table 8.1 should not be used for dilution rates in excess of 10%/hour.

The following example illustrates the use of the rollback procedure with the information in Table 8.1

Example 1

Given:

- Hourly NO_2 concentration = 0.30 ppm
- Prevailing $NMOC/NO_x$ ratio on days with high hourly NO_2 = 9:1
- In the absence of further controls, a projected increase in NO_x emissions of 20% over a defined period (e.g., 1987)
- An existing ozone SIP requiring 40% reduction in VOC over the same defined period (i.e., 1987).

Find:

The required reduction in NO_x emissions to meet a hypothetical hourly NAAQS for NO_2 of 0.25 ppm not expected to be exceeded more than once per year.

Table 8.1. Sensitivity of Peak NO_2 to Changes in NMOC with Various Prevailing $NMOC/NO_x$ Ratios

Ratio*	% Reduction in Peak NO_2 Accompanying a 50% Reduction in NMOC
>10:1	0%
8-10:1	10%
6-8:1	15%
4-6:1	20%

* If the prevailing $NMOC/NO_x$ ratio is not known on days experiencing NO_2 in excess of the air quality control, assume 0% reduction in peak NO_2 resulting from reductions in NMOC.

Solution:

(1) Estimate future NO_2 design value which would occur in the absence of further controls

$$x_f = (0.30)(1.20) \qquad (8.1)$$

$$x_f = 0.36 \text{ ppm}^*$$

(2) Reduce the future design value consistently with the prevailing $NMOC/NO_x$ ratio. According to Table 8.1, for a VOC/NO_x ratio of 9:1, a 50% reduction in NMOC results in a 10% reduction in peak NO_2. Since the anticipated reduction in VOC emissions is 40% rather than 50%, reduce the future design value as shown:

$$\text{Reduction due to VOC Reduction} = \left(\frac{40}{50}\right)(10) = 8\%$$

$$\text{New } NO_2 \text{ Design Value} = (0.36)\ (1.00 - .08)$$

$$= 0.33 \text{ ppm}$$

(3) Estimate the required reduction in projected NO_x emissions (Q_{future}) needed to attain the NAAQS at the end of the period of interest (e.g., 1987).

$$R = \left[\frac{0.33 - 0.25}{0.33}\right] \times 100 \qquad (8.2)$$

$$R = \underline{24\%}$$

The procedure illustrated in Example 1 is not appropriate in the unusual case when NO_2 occurs as the result of ozone-limited titration in the absence of carryover NO_2. In such a case, it would be necessary to estimate reductions in ambient ozone using models which have been described elsewhere.[22,23,31] In the absence of better information, the resulting reduction in peak NO_2 would be proportional to the estimated reduction in peak ozone, after making some allowance for NO_x which is emitted directly as NO_2. The procedure is illustrated in Example 2.

---

* Note that the calculations should not be carried out to more than two significant figures.

Example 2

Given:

(1) An NO_2 Design Value = 0.30 ppm is observed which is primarily attributable to ozone-limiting titration occurring in the absence of carryover NO_2.

(2) A VOC emission control program is estimated to reduce peak ozone by 30%.

Find:

The resulting reduction in peak NO_2.

Solution:

(1) Assume 10% of the NO_2 results from direct emission of NO_2

(.10)(.30 ppm) = .03 ppm of NO_2 would not be affected by reducing ozone

(2) This leaves 0.27 ppm NO_2

$$\text{Estimated Future } NO_2 = (0.27)(1-.30) + .03$$

$$= 0.22 \text{ ppm}$$

Information presented in Chapter 7.0 casts serious doubt concerning the validity of the rollback model's assumption that the relative contribution a source category makes to ambient concentrations is the same as its relative contribution to total NO_x emissions. As discussed in Chapter 7.0, monitoring data seldom appear to reflect impacts from major point sources. This could result in credibility problems if the rollback model is used as the basis for applying controls on a large source which does not impact the monitoring site. Failure to observe subsequent improvement in ambient NO_2 after implementation of controls could cause criticism of a strategy to reduce emissions from such sources. Criticism of this nature may stem solely from improper use of the rollback model rather than from the effectiveness of the strategy per se. A similar problem may occur if the rollback model is used to assess the impact of a transportation control measure which is applied at one or a few sites which either do not impact monitoring sites or have a disproportionately high impact on a monitor site (e.g., as may be the case if a roadway near a monitor were turned into a pedestrian mall). Thus, the rollback model is most suitable for estimating the impact of controls which are applied uniformly to ubiquitous sources. Examples of such strategies include the Federal Motor Vehicle Control Program (FMVCP) and inspection and maintenance programs.

The impact of widespread control programs (e.g., inspection and maintenance) on observed peak and mean concentrations of NO_2 may be underestimated using the rollback model unless emissions from large, elevated point sources are somehow discounted. Use of available SO_2 data (see Chapter 7.0) as a tracer for NO_2 originating from large, elevated stationary combustion sources can be used as justification for discounting such emissions. If (1) NO_x emissions from large point sources with elevated stacks is accompanied by SO_2 emissions, and (2) ambient data indicate no correspondence between peak NO_2 and observed ambient SO_2 patterns, NO_x emissions from large elevated point sources can be eliminated from the "Q" terms on the right hand side of Equation (8.1). Because of the unlikelihood of observing an impact from an elevated source at any given point, in applying the rollback model, NO_x emissions can be eliminated from the "Q" terms on the right hand side of Equation (8.1) in estimating controls needed to meet the annual NO_2 standard regardless of whether there are any SO_2 data.

It should be emphasized that the suggestions in the previous paragraph are intended to insure that the rollback model provides estimates which result in more credible prescriptions for ubiquitously applied control measures. The suggestions do not imply that elevated point sources of NO_x are unimportant. If elevated point source emissions are eliminated from the rollback model as suggested, their potential impact on peak NO_2 values needs to be considered in some other way. However, it is first necessary to describe available models for estimating the impact from point sources. Therefore, the discussion of appropriate procedures for supplementing the rollback model to consider point sources will be deferred until Section 8.2.

Because the impact of elevated point sources are not ordinarly expected to impact appreciably on annual average NO_2 concentrations at any given site, it is sufficient to use Equations (8.1) and (8.2) to estimated needed NO_x emission controls excluding emissions from elevated point sources. It is not ordinarily necessary to supplement this analysis with applications of a point source model in this case.

8.1.2 OZIPM

The OZIPM (Modified Ozone Isopleth Plotting Package) is similar conceptually to the OZIPP/EKMA model described extensively elsewhere.[22,23,31] A well-mixed column of air is assumed to migrate within an urban area so that it encompasses the monitoring site observing the peak NO_2 concentration at the time of the observation. This is pictured conceptually in Figure 8.1. The OZIPM model provides the user with a graph of peak hourly NO_2 (rather than O_3) as a function of initial NMOC and NO_x concentrations. Figure 6.5 (page 62) is an example of such a diagram. The positions of the NO_2 isopleths are also functions of the NO_x and VOC emissions encountered by the column along its trajectory, diurnal variation in the mixing height, sunlight intensity and ozone transported from upwind. As with the EKMA procedure, one uses 6-9 a.m. NMOC/NO_x ratios and the peak observed NO_2 concentration to identify a starting point on the isopleth diagram. Control requirements needed to attain a specified air quality goal are calculated from the starting point.

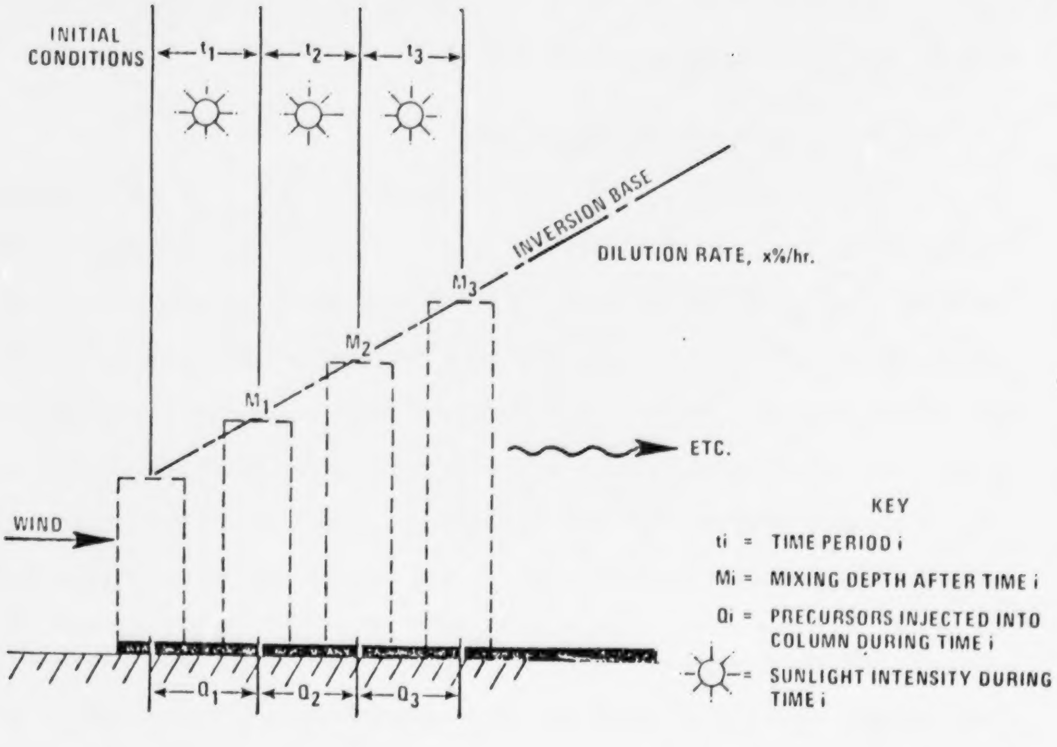

INITIAL CONDITIONS
t1
t2
t3
INVERSION BASE
DILUTION RATE, x%/hr.
M3
M2
M1
ETC.
WIND
Q1
Q2
Q3
KEY
ti = TIME PERIOD i
Mi = MIXING DEPTH AFTER TIME i
Qi = PRECURSORS INJECTED INTO COLUMN DURING TIME i
= SUNLIGHT INTENSITY DURING TIME i

Figure 8.1 Conceptual view of the column model.

The OZIPM model has several potential advantages over rollback. First, the isopleth diagram can be applied to cases in which NO_2 results from either synthesis or titration. Second, the impact of VOC emission controls on peak NO_2 can be more readily determined. The problem with uniform distribution of point sources still remains however. Other problems are that the OZIPM model is only appropriate for short term NO_2 concentrations and its applicability to winter NO_2 episodes is uncertain. Finally, and most importantly, the model needs to be further evaluated. Thus, it is not expected to be widely available for use in control strategy evaluations until late 1981.

8.1.3 Photochemical Box Model (PBM)

The PBM model has been recently developed and is currently undergoing further evaluation. In this model, a large stationary cell is superimposed over the urban area as shown in Figure 8.2.[32] The change in estimated pollutant concentrations with time is dependent upon the flux of emissions within the box, the inflow and outflow of pollutants, the dilution which occurs as the mixed layer rises, entrainment of species from aloft and formation and destruction of species through chemical reaction. The model assumes that all emissions are instantaneously mixed throughout the box and ignores horizontal dispersion.

The model requires overall urban emissions of CO, VOC (divided into five classes), and NO_x for each hour of the modeling period (i.e., 0500 to 1700). No spatial resolution of emissions is required. The output gives a single city-wide prediction for each pollutant for each hour in the modeling period. The box model has been exercised using several days during the summer of 1976. Air quality data from twelve monitoring sites were used in comparing predicted and observed concentrations. The comparison showed generally good

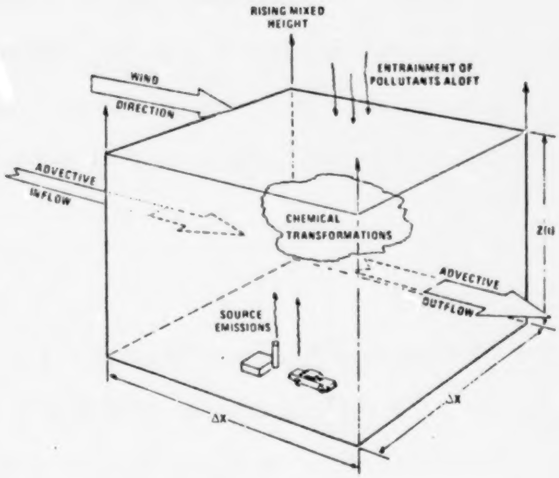

RISING MIXED HEIGHT
ENTRAINMENT OF POLLUTANTS ALOFT
WIND DIRECTION
ADVECTIVE INFLOW
CHEMICAL TRANSFORMATIONS
Z(t)
ADVECTIVE OUTFLOW
SOURCE EMISSIONS
Δx
Δx

Figure 8.2 Schematic diagram of modeling domain for the Photochemical Box Model.

agreement between predicted and observed concentrations of CO, NO, NO_2 and O_3 averaged among numerous monitoring sites within a city.[32]

The PBM has many of the same advantages and problems as the OZIPM model. An additional advantage is that it is not dependent on the proper location of NO/NO_x monitors. One problem with the Box Model which has yet to be solved is that it predicts the spatially averaged NO_2 concentration throughout the box. A way must be found to relate this spatial average to peak NO_2 concentrations for the model to be directly usable to assess the impact of controls to reduce high short term concentrations of NO_2. It is not certain whether or when this latter difficulty can be overcome.

8.1.4 Complex Multisource Models

This section identifies models which are distinctive from those described in Sections 8.1.1 - 8.1.3 in that they reflect greater attempts to incorporate physical/chemical phenomena believed to occur in urban areas. However, any resulting increase in credibility occurs at the expense of increased data and computer requirements for running the model. Unless a suitable data base has already been compiled for ozone modeling, it is not likely that such models can be exercised to assess the effectiveness of control strategies to reduce NO_2 without a lengthy and expensive effort to assemble an adequate data base. Table 8.2 identifies the complex multisource photochemical models discussed in greater detail in Reference 33.

8.2 Models to Assess the Impact from Individual Sources

The models identified in Section 8.1 have been primarily used to estimate the impact of numerous rather than individual sources. Simple models like rollback which have no spatial resolution are not well suited for estimating the

Table 8.2. Available Complex Multisource Photochemical Dispersion Models

Model	Type	Additional References
ELSTAR	Trajectory	34
IMPACT	Grid	35
LIRAQ-2	Grid	36, 37
MADCAP	Grid	38, 39
TRACE	Trajectory	40, 41
URBAN AIRSHED	Grid	42

impact of an individual source. Monitoring data collected in the vicinity of large sources of NO_x suggest that, at any given time, the maximum impact of an individual source may be quite localized. For example, Figure 7.9a (page 87) shows that the plume width from the Labadie power plant is only about 4 km across as far as 21 km downwind from the plant.[25] As shown in Figure 8.3, Cole _et al_. found that the identifiable impact on NO_2 of a major freeway occurred within a few hundred meters of the roadway.[43] Even the most complex multisource grid models typically have no greater horizontal spatial resolution than 2-4 km. This limitation is necessary in order to assure computational feasibility. Consequently, models which focus on individual sources may be useful for new source review or, if it is desirable, to assess the impact of controlling a major source in the vicinity of that source.

Cole and Summerhays have described several different approaches which have been used to estimate NO_2 concentrations in point source plumes.[44] In addition, Cole _et al_. have applied a relatively simple approach to estimate NO_2 concentrations downwind from a major freeway with some success.[43] Only the more simple approaches will be described herein. Information concerning a refined reactive plume model is available in Reference 45.

The principal distinguishing feature between simple and complex models for individual sources of NO_x is that simple approaches do not account for the interaction of the NO_x plume with organic pollutants. However, this limitation is not a serious one insofar as predicting peak NO_2 is concerned. A number of field investigations have indicated that peak NO_2 within an identifiable plume of an individual source occurs far too rapidly for reactions with organic pollutants to cause a significant part of the problem.[25,26,27,43] Further, several of the

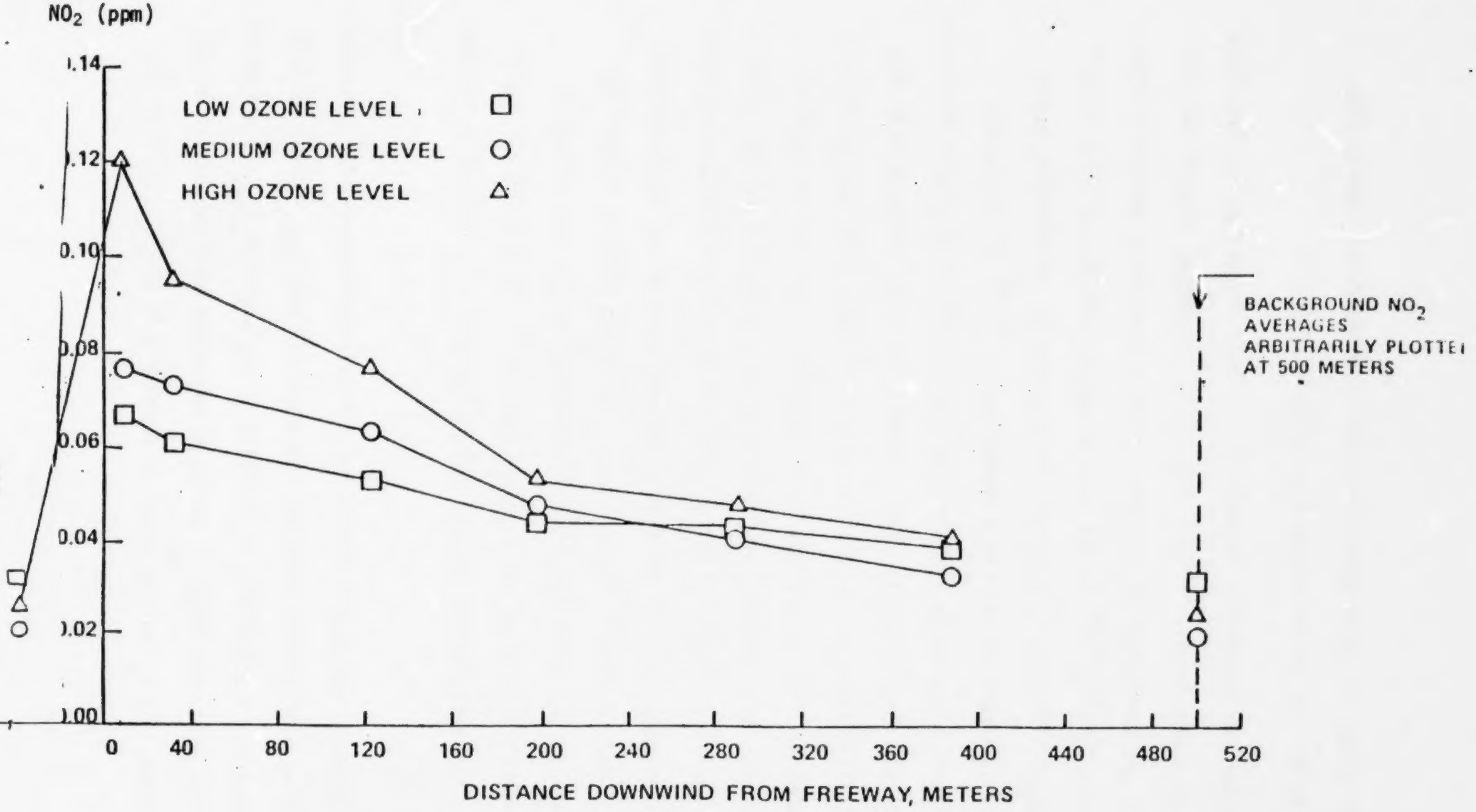


Figure 8.3 Nitrogen dioxide (NO_2) data from the NO_2/O_3 sampler siting study.

simple approaches appear to agree quite well with observed data. Hence, they should be adequate for use in evaluating NO_2 control strategies.

Four approaches are identified in Table 8.3. These approaches are described in detail in several references.[26,44,45] All of the approaches require the user to first estimate maximum hourly NO_x concentrations using widely available models for inert pollutants.[46,47,48,49] In the case of major roadways, a "line source" model such as HIWAY[47,48] would be used for these purposes. Appropriate point source models are available on the EPA's UNAMAP system.[46,47] Of the models described in Table 8.3, the Ozone-Limiting and the Photostationary State Approaches are preferable to the others, because they consider the limitations on peak NO_2 posed by the oxidizing potential of dilution air. The Ozone-Limiting Approach is more practical than the Photostationary State Approach because of the general lack of rate constant data available to persons likely to be formulating control strategies. Preliminary testing of the Ozone-Limiting Approach and several other NO_2 models for individual sources has been performed using aircraft measurements of power plant plumes in the St. Louis region. The Ozone-Limiting Method was found to be reasonably accurate and performed slightly better than a complex reactive plume model, as well as other simple models.[50] Consequently, a recommended procedure for applying the Ozone-Limiting Approach is presented in greater detail.

The ozone-limiting approach involves two initial comparisons: (1) comparison of the estimated maximum ground level NO_x concentration $[NO_x]_{max}$ and the maximum ambient O_3 concentration prevailing at the time of day when $[NO_x]_{max}$ is estimated, and (2) comparison estimated $[NO_x]_{max}$ during midafternoon with prevailing ozone levels at that time. If O_3 concentration is greater than $[NO_x]_{max}$, all of the

TABLE 8.3 Approaches for Estimating Maximum Impact on Peak NO_2 from Large Individual Sources

Name	Description	Remarks
1) Partial Conversion	1) Multiply predicted maximum NO_x concentration by a constant factor to predict peak NO_2.	1) It is difficult to determine what the factor should be. Ambient measurements of NO_2/NO_x ratios within plumes vary widely. (See Fig. 7.6) Generally, the greater the dilution, the higher the ratio. As a rule, routinely collected monitoring data are not useful for these purposes, because they do not reflect the impact of point sources. Monitoring data collected in the vicinity ~200m of a major roadway may be of use for roadway applications.
2) Exponential Decay	2) Multiply predicted NO_x concentrations by an exponential decay factor $NO_2 = (rb)(NO_x)(1-e^{.693t/\tau}) + (b)(NO_x)$ where t = travel time from source, time center T = half life conversion time of NO to NO_2, consistent units b = fraction of NO_x emitted as NO_2, assumed to be 0.10 for combustion sources, could be higher for industrial process sources. $(NO_x)_{max}$ = Maximum estimated ground level concentrations of NO_x using an inert pollutant model.	2) Conversion of NO to NO_2 appears to be limited by the oxidizing potential of the dilution air. Also, the half life of the NO is determined by dilution rather than chemistry. Any value chosen for the half life would have to be arbitrary.
Name	Description	Remarks
3) Ozone Limiting Approach	3) Method assumes that maximum NO_2 concentration can be limited by dilution of an NO_x plume and/or the ozone concentrations in the dilution air. If ozone is the limiting factor, $[NO_2]_{max} = [O_3]_t = [NO_x]_{max}$ where $[O_3]_t$ = ambient ozone concentrations at the time peak NO_2 occurs. b = fraction of NO_x emitted as NO_2 $[NO_x]_{max}$ = Maximum ground level NO_x estimated with an inert point source model.	3) As discussed in Chapter 7.0, the summation of $(NO + NO_2 + O_3)$ appears to be constant across point source plumes (see Figures 7.9 and 7.10). This implies that NO to NO_2 conversion in plumes with high NO_x is limited by prevailing ambient ozone. Fewer arbitrary assumptions are required using this method than methods (1) or (2). Method assumes that complete mixing of the NO_x plumes occurrs at the point where maximum ground level NO occurs. It also ignores the likelihood of further photodisassociation of NO_2 upon formation. Measurements or estimates of prevailing ambient O_3 levels at the time $(NO_x)_{max}$ occurs are needed.
4) Photostationary State Approach	4) Approach combines $(NO_x)_{max}$ estimated with an inert pollutant model with the photostationary state relationship. As a result, $[NO_2]_{max}$ is estimated as follows: $[NO_2]_{max} = \frac{k_3 [O_3] [NO_x]_{max}}{[k_1 + k_3[O_3]]}$ where $[NO_x]_{max}$ = peak ground level NO_x concentrations estimated with a model for inert pollutants k_1 = the ratio constant in reaction with which NO_2 photodisassociates in the presence of sunlight: $NO_2 \xrightarrow[K_1]{h\nu} NO + O$ k_3 = rate constant depicting the rate with which O_3 combines with NO to form NO_2: $NO + O_3 \xrightarrow[k_3]{} NO_2 + O_2$	4) White[26] and Cole *et al.*[43] have found this approach to work well in predicting maximum NO_2 downwind from a major point source and a major line source. The approach assumes thorough mixing of the plumes with ambient air at the point where $(NO_x)_{max}$ occurs. Measurements of the k_1 rate constant are not typically available. The approach also requires measurement of prevailing O_3 concentrations at the time $(NO_x)_{max}$ occurs.

NO_x is assumed to be NO_2. If $[NO_x]_{max}$ is greater than the prevailing O_3 concentration, NO_2 formation is "ozone-limited." In this latter case, the maximum NO_2 concentration is assumed to be equal to the O_3 concentration plus a correction factor which accounts for NO_x emitted as NO_2 and near-stack thermal conversion. For combustion sources, the correction factor is assumed to be 10 percent of the estimated $[NO_x]_{max}$. The Ozone-Limiting Procedure is outlined in four steps below.

1. A standard dispersion model for inert pollutants is used to calculate $[NO_x]_{max}$.

2. $[NO_x]_{max}$ is separated into two components:

a) portion emitted as NO_2 or thermally converted, equal to $b \cdot [NO_x]_{max}$, where "b" is assumed to be .10 for combustion sources;

b) the remaining NO_x is assumed to be NO subject to conversion by O_3. This NO is $(1-b)[NO_x]_{max}$ or $.90[NO_x]_{max}$ for combustion sources.

3. a) If $[O_3] > (1-b)[NO_x]_{max}$, then assume that all of the NO is converted to NO_2 (i.e., $[NO_x]_{max} = [NO_2]_{max}$).

b) If $(1-b)[NO_x]_{max} > [O_3]$, then

$$[NO_2]_{max} = [O_3] + (b)\,[NO_x]_{max}.$$

This procedure should be used to address two situations: (i) when NO_x is maximum, and (ii) when O_3 is maximum. Note that the above procedure can also be readily applied to assess the impact from other industrial point sources (e.g., nitric acid plants, natural gas pumping compressor stations) which emit a larger fraction of NO_x as NO_2. One would simply increase the "b" value, described in step 2a), to whatever fractional value is appropriate for these sources.

The procedure is illustrated with two examples.

Example 3a

Given: A point source dispersion model for inert pollutants estimates $[NO_x]_{max} = 0.30$ ppm to occur in midmorning as the result of fumigation of a power plant's plume. Existing ozone monitors suggest that the highest O_3 concentration for this time of day is 0.10 ppm.

Find: Maximum impact of the point source on hourly ambient NO_2 levels.

Solution:

(1) Since a power plant is a combustion source, assume b = 0.10

(2) Since $(0.90)[NO_x]_{max} = 0.27\text{ppm} > 0.10 \text{ ppm} = [O_3]$,

$[NO_2]_{max}$ is ozone-limited

(3) $$[NO_2]_{max} = [O_3] + b \cdot [NO_x]_{max}$$

$$= 0.10 + (.10)(.30)$$
$$= 0.13 \text{ ppm}$$

Example 3b

Given: For the power plant in Example 3a, $[NO_x]_{max}$ for midafternoon is estimated to be 0.15 ppm. Peak ozone at this time is measured to be 0.20 ppm.

Find: Maximum impact of the point source on hourly ambient NO_2 levels.

Solution:

(1) b = 0.10

(2) $(1\text{-}b)\ [NO_x]_{max} = (.90)(.15) = 0.14 \text{ ppm} < 0.20 = [O_3]$

Therefore, $[NO_2]$ max is NO_x limiting

(3) $[NO_2]_{max} = [NO_x]_{max} = 0.15$ ppm

One additional facet of modeling procedures for NO_2 needs to be discussed. This is the integration of multisource and individual source techniques described in Sections 8.1 and 8.2, respectively. In the complex multisource models enumerated in Section 8.1.4, this integration has already occurred. That is, these models already include both area and point sources in their emission inventories. Because complex models can more accurately simulate source-receptor relationships, the impact of elevated sources on groundlevel concentrations have a greater chance of being correctly estimated. The only occasion when it may be desirable to separate a point source from an inventory used in a complex multisource model would be if one were interested in assessing the microscale impact of a particular individual source. In such a case, the procedure would be to:

(1) eliminate that particular source from the inventory;

(2) use the multisource model to estimate NO, NO_2 and ozone concentrations attributable to all other sources;

(3) apply an individual source model (e.g., the Ozone-Limiting Approach) to simulate the impact of the source of interest, using the multisource model's estimates as the means for characterizing the oxidizing potential of the dilution air.

In order for the rollback model to be an acceptable approach for estimating the impact of control strategies on peak short term NO_2 concentrations, it is necessary to account for source-receptor relationships in some rudimentary way. As discussed in Section 8.1.1, it will usually be appropriate to exclude elevated point sources from the inventory in applying the rollback model to short term situations. If this is done, however, use of the rollback model in individual areas needs to be supplemented by separate consideration of large individual sources not impacting a monitoring site. The recommended procedure is as follows.

(1) Review available SO_2 and NO_2 data on occasions with high NO_2 using techniques described in Chapter 7.0.

a. If there is a clear correspondence between NO_2 and SO_2 peaks, include emissions from elevated point sources in the emission terms on the right-hand-side of Equation (8.1). Estimate required controls using Equation (8.2).

b. Otherwise, project future NO_2 concentrations using Equation (8.1) excluding elevated point source emissions from the emission terms. Proceed to step (2).

(2) Apply the Ozone-Limiting Approach to estimate peak impact of selected large individual sources on ground level NO_2.

(3) Repeat (2) for several scenarios as needed (e.g., fumigation case, afternoon impact during periods with maximum O_3, etc.).

(4) Repeat (1)(b) using NO_2 design values which are appropriate for the times of day assumed for each scenario in (3) and occur nearest to the location where the peak industrial source impact occurs. If there are no monitoring data near this location, use a spatially averaged value for the appropriate time of day.

(5) For each scenario assumed in steps (3) and (4), superimpose the estimated peak point source impact on the projected future level of NO_2 obtained with the rollback model.

The foregoing procedure is illustrated numerically in Table 8.4.

8.3 Implications

1. Two major categories of models have been discussed: multisource models and individual source models. In order to provide comprehensive quantitative estimates of controls needed to attain a short term air quality goal for NO_2, both kinds of models need to be utilized. In designing control strategies to meet an annual NO_2 air quality goal, it is generally sufficient to utilize multisource models alone. If rollback is the multisource model utilized, emissions from large individual point sources may be ignored in applying the model to estimate the impact of controls in a achieving annual average air quality goals.

2. Although several multisource models exist, the one that is most widely available and easiest to apply is the linear rollback model. Rollback is suitable for use in both annual and short term applications. Peak and mean NO_2 concentrations appear to be proportional to NO_x under most circumstances. Consideration of the impact of reducing NMOC can be made by supplementing the rollback model as illustrated in Example 8.2 (Section 8.1.1).

3. Several relatively simple approaches for estimating the maximum impact from large individual sources of NO_x (e.g., a public utility or a major highway) have been described in Section 8.2. Of these, the Ozone-Limiting Approach appears to represent the best available compromise between accuracy and data requirements. This approach is also readily adaptable for modeling sources which emit large proportions of NO_x directly as NO_2.

TABLE 8.4 Hypothetical Examples Illustrating Use of Multi and Individual Source Models for Projecting Future Short Term NO_2 Concentrations for Use in SIP's

Scenario	Time of Day	Estimated Peak Individual Source Contribution	Projected Multi-Source Contribution	Projected Peak NO_2
1) Observed nighttime-early morning peaks. Impact from elevated point source assumed to be negligible due to nocturnal inversion.	1900-0800	0	0.30 ppm	0.30 ppm
2) Observed mid-morning peaks. Multisource synthesis of NO_2 superimposed by fumigation impact from an elevated point source.	0900-1100	0.13 ppm	0.20 ppm	0.33 ppm
3) Observed mid-afternoon peaks. Potential point source impact is relatively high due to high observed O_3 levels at this time. Projected multisource impact is low due to low NO_2 concentrations observed by existing monitors during this time.	1200-1800	0.15 ppm	0.06 ppm	0.21 ppm

4. Where available, SO_2 data should be used to verify the impact of large stationary point sources on high observed hourly concentrations of NO_2 using the procedure outlined in Chapter 7.0. In cases where a review of available evidence indicates a lack of point source impact, NO_x emissions from major elevated point sources should be eliminated from the emission inventory when using rollback. Peak impacts on NO_2 estimated from large individual sources with the Ozone-Limiting Approach should be superimposed on projected NO_2 concentrations thus obtained with the rollback model. This procedure is illustrated more completely by the flow chart in Figure 8.4.

5. The procedure described in paragraph 4 can be repeated for several scenarios using consistent estimates of impacts from multiple sources and large individual sources. An example of several scenarios is illustrated in Table 8.4. Such repetition should better insure protection of the public against excessively high short term exposure to NO_2.

6. To be implemented, the procedure outlined in paragraphs 4 and 5 requires several pieces of data and judgments to be made which may not at first be obvious.

a. A certain amount of expertise regarding local meteorological conditions is needed in order to arrive at a realistic set of scenarios.

b. Measurements of peak hourly NO_2 concentrations and ozone at times of day which are consistent with selected scenarios need to be made at monitoring sites which are likely to represent NO_2 levels encountered in widespread areas of the city.

c. It is desirable, but not essential, to have estimates of the prevailing $NMOC/NO_x$ ratio in the city being modeled.

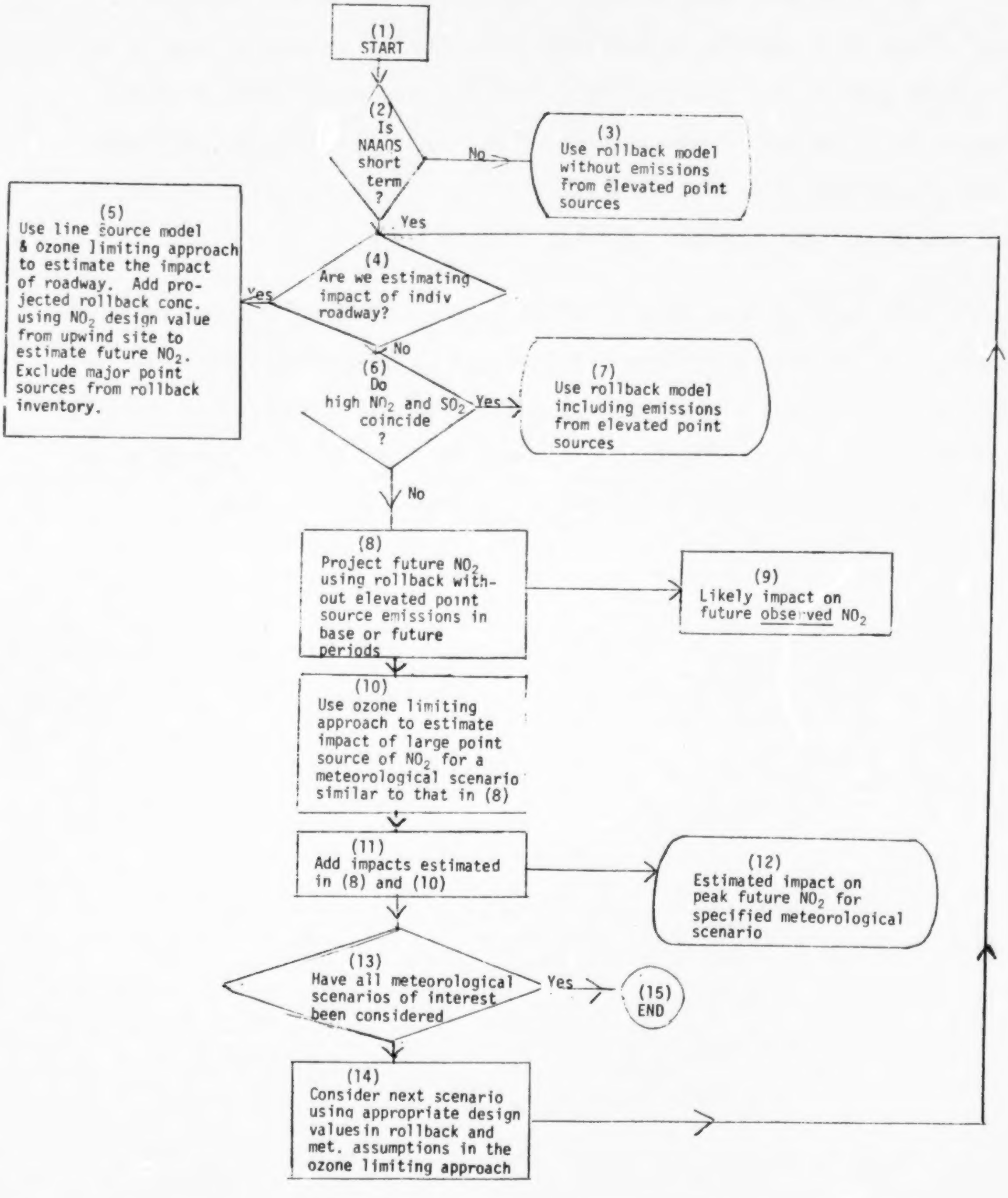

(1) START
(2) Is NAAQS short term ?
No
(3) Use rollback model without emissions from elevated point sources
Yes
(4) Are we estimating impact of indiv roadway?
Yes
(5) Use line source model & ozone limiting approach to estimate the impact of roadway. Add projected rollback conc. using NO₂ design value from upwind site to estimate future NO₂. Exclude major point sources from rollback inventory.
No
(6) Do high NO₂ and SO₂ coincide ?
Yes
(7) Use rollback model including emissions from elevated point sources
No
(8) Project future NO₂ using rollback without elevated point source emissions in base or future periods
(9) Likely impact on future observed NO₂
(10) Use ozone limiting approach to estimate impact of large point source of NO₂ for a meteorological scenario similar to that in (8)
(11) Add impacts estimated in (8) and (10)
(12) Estimated impact on peak future NO₂ for specified meteorological scenario
(13) Have all meteorological scenarios of interest been considered
Yes
(15) END
(14) Consider next scenario using appropriate design values in rollback and met. assumptions in the ozone limiting approach

Figure 8.4. Procedure for Applying Rollback in Assessing the Impact of Control Strategies on NO_2

d. A judgment needs to be made about future prevailing levels of ozone. Since it is anticipated that areas violating any prospective short term air quality goal for NO_2 are also likely to violate the hourly NAAQs for ozone, estimates of future peak afternoon ozone values should be available. Estimates of future nighttime or morning ozone concentrations should be consistent with those made about future transported ozone in ozone SIP's.

7. The modeling approaches described in this chapter imply that it may be possible to estimate a prospective violation of a short term NO_2 NAAQS even though one has not been observed and may not be likely to be observed by existing monitoring networks. For example, if an hourly NO_2 NAAQS of 0.25 ppm were established, hypothetical Scenario 2 in Table 8.4 would be a case in point.

9.0 REFERENCES

1. *National Air Quality, Monitoring, and Emissions Trends Report 1977*, EPA-450/2-78-052, pages 5-11, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1978.

2. *Air Quality Criteria for Oxides of Nitrogen* (draft), Chapter 6, revised June 1980.

3. J. R. Martinez, *Survey of the Role of NO_x in Nonurban Ozone Formation*, EPA-450/4-79-035, September 1979.

4. National Emissions Data System (NEDS), National Air Data Branch, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

5. Research Triangle Institute (1975), *Investigation of Rural Oxidant Levels as Related to Urban Hydrocarbon Control Strategies*, EPA-450/3-75-036, March 1975.

6. C. E. Decker, *et al.*, *Formation and Transport of Oxidants Along the Gulf Coast and in Northern U.S.*, EPA-450/3-76-033, August 1976.

7. W. C. Eaton, C. E. Decker, J. B. Tommerdahl, F. E. Dimmock, *Study of Nature of Ozone, Oxides of Nitrogen and Nonmethane Hydrocarbons in Tulsa, Oklahoma*, Research Triangle Institute, RTI/1466/000, F. April 1979.

8. SAROAD, 1975-1977, *SAROAD Data Summaries*, maintained by National Air Data Branch, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

9. J. R. Martinez, K. C. Nitz, *Analysis of High NO_2 in California, 1975-1977*, EPA-450/4-79-034a, b, c, August 1979.

10. SAROAD 1975-1977, SAROAD Hourly Concentrations, maintained by National Air Data Branch, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

11. D. H. Sennett, personal communication concerning a Brief Analysis of LACS Data Base, LACS Study, summer 1978, Los Angeles, California.

12. Personal communication of A. J. Hoffman to J. D. Sableski, subject "NO_2 Siting Guidance," July 14, 1978.

13. U.S. Environmental Protection Agency, "Ambient Air Quality Monitoring, Data Reporting and Surveillance Provisions," *Federal Register* (40CRF 51,52,53,58), *44* No. 92 (May 10, 1979), pp. 27558-27604.

14. T. C. Curran, *Screening Procedure for Ambient Air Quality Data*, EPA-450/2-78-037, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1978.

15. H. G. Richter, E. L. Meyer, and D. H. Sennett, "A Graphical Procedure for Screening and Analyzing High NO_2 Concentrations," *Paper 79-12.4*, presented at 72nd APCA Meeting, Cincinnati, Ohio, June 1979.

16. C. W. Spicer, *The Fate of Nitrogen Oxides in the Atmosphere*, EPA-600/3-76-030, March 1976.

17. C. W. Spicer, D. W. Joseph, P. R. Sticksel, G. M. Sverdrup, and G. F. Wood, *Reactions and Transport of Nitrogen Oxides and Ozone in the Atmosphere*, draft, EPA Contract 68-02-2439, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1979.

18. C. W. Spicer, J. R. Koetz, G. W. Keigley, G. M. Sverdrup, and G. F. Wood, *A Study of Nitrogen Oxide Reactions Within Urban Plumes Transported Over the Ocean*, draft, EPA Contract No. 68-02-2957, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1979.

19. J. C. Trijonis, T. K. Peng, G. J. McRae, and L. Lees, *Emissions and Air Quality Trends in the South Coast Air Basin*, EQL Memo No. 16, January 1976, California Institute of Technology, Pasadena, California.

20. J. C. Trijonis, "Dependence of Ambient NO_2 on Precursor Control," paper presented at *EPA Technical Symposium on Implication of a Low NO_x Vehicle Emission Standard*, May 2-4, 1979, Reston, Virginia.

21. J. C. Trijonis, *Empirical Relationships Between Atmospheric Nitrogen Dioxide and Its Precursors*, EPA-600/3-78-018, February 1978.

22. *Uses, Limitations, and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors*, EPA-450/2-77-021a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, November 1977.

23. *Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors: Supporting Documentation*, EPA-450/2-77-021b, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1978.

24. R. B. Evans, *The Contribution of Ozone Aloft to Surface Ozone Maxima*, PhD Dissertation, University of North Carolina, Chapel Hill, North Carolina, 1979.

25. W. H. White, J. A. Anderson, W. R. Knuth, D. L. Blumenthal, J. C. Hsiung, and R. B. Husar, *Midwest Interstate Sulfur Transformation and Transport Project: Aerial Measurements of Urban and Power Plant Plumes, Summer 1974*, EPA-600/3-76-110, November 1976.

26. W. H. White, *NO_x - O_3 Photochemistry in Power Plant Plumes: Comparison of Theory with Observation*, Environmental Science and Technology II (10) October 1977, page 995.

27. D. Hegg, P. V. Hobbs, L. F. Radke, and H. Harrison, "Reactions of Ozone and Nitrogen Oxides in Power Plant Plumes," Atmospheric Environment 11, (6), page 521.

28. Acurex Corporation, Control Techniques for Nitrogen Oxides Emissions from Stationary Sources - 2nd Edition, EPA-450/1-78-001, January 1978.

29. N. deNevers and J. R. Morris, "Rollback Modeling: Basic and Modified," JAPCA 25, page 943, September 1975.

30. J. H. Wilson, Jr., "Methodologies for Projecting the Relative Air Quality Impacts of Emission Control Strategies," Paper 78-4.1, presented at 71st Annual Air Pollution Control Association Meeting, Houston, Texas, June 1978.

31. G. Z. Whitten and H. Hogo, User's Manual for Kinetics Model and Ozone Isopleth Plotting Package, EPA-600/8-78-014a, July 1978.

32. K. L. Schere and K. L. Demerjian, "A Photochemical Box Model for Urban Air Quality Simulation," Proceedings 4th Joint Conference on Sensing of Environmental Pollutants, American Chemical Society, 1978.

33. R. Y. Wada, M. J. Wong, and E. Y. Leong, Applicability of Selected Models for Addressing Ozone Control Strategy Issues, EPA-450/4-79-026, December 1979.

34. F. Lurmann, D. Godden, A. C. Lloyd, and R. A. Nordsieck, A Lagrangian Photochemical Air Quality Simulation Model, EPA-600/8-79-015a, b, June 1979.

35. A. Fabrick, R. C. Sklarew and J. G. Wilson, "Point Source Model Evaluation and Development Study, Appendix C, User Guide to Impact," prepared for California Air Resources Board and the California Energy Resources Conservation and Development Commission by Science Application, Incorporated, Westlake Village, California, SAI Contract No. A5-058087, March 1977.

36. M. C. MacCracken, et al., "The Livermore Regional Air Quality Model: I. Concept and Development," Journal of Applied Meteorology 17, March 1978, pages 254-272.

37. W. H. Duewer, et al., "The Livermore Regional Air Quality Model: II. Verification and Sample Application in the San Francisco Bay Area," J. Applied Meteorology 17, March 1978, pages 273-311.

38. R. C. Sklarew, M. A. Joncich, and K. T. Tran, "An Operational Air Quality Modeling System for Photochemical Smog in the San Diego Air Basin," presented at the Annual American Meteorological Society Meeting, Reno, Nevada, January 1979.

39. R. C. Sklarew, "Verification of the MADCAP Model of Photochemical Air Pollution in the San Diego Air Basin," presented at the Annual American Meteorological Society Meeting, Reno, Nevada, January 1979.

40. P. J. Drivas, "TRACE (Trajectory Atmospheric Chemistry and Emissions) User's Guide," Pacific Enivronmental Services, Incorporated, Santa Monica, California, PES Report TPT016, November 1977.

41. P. J. Drivas and L. G. Wayne, "Validation of an Improved Photochemical Air Quality Simulation Model," Pacific Environmental Services, Incorporated, Santa Monica, California, PES Report TP-014, March 1977.

42. S. D. Reynolds, L. E. Reid and T. W. Tesche, "An Introduction to the SAI Airshed Model and Its Usage," Systems Applications, Incorporated, San Rafael, California, SAI Report EF 78-53R, December 1978.

43. H. S. Cole, N. Mayer, and H. Fowler, "The Impact of an NO_x Diesel Waiver on NO_2 Concentrations Downwind of a Major Line Source," U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, internal report, May 1979.

44. H. S. Cole and J. E. Summerhays, "A Review of Techniques Available for Estimating Short Term NO_2 Concentrations," *JAPCA* *29* (8), August 1979, pages 812-817.

45. D. Stewart and M. A. Yocke, *User's Guide to the Reactive Plume Model - RPM-II*, SAI Report EI-79-93R, EPA Contract No. 68-02-2775 (1980) in press.

46. C. Hosler, "Meteorological Program of the Environmental Protection Agency, *Bull American Meteorological Society* *56* (12), December 1975, pages 1261-1270.

47. D. B. Turner, "Atmospheric Dispersion Modeling: A Critical Review," *JAPCA* *29* (5), May 1979, pages 502-519.

48. J. R. Zimmerman and R. S. Thompson, *User's Guide for HIWAY, A Highway Air Pollution Model*, EPA-650/4-74-008, February 1975.

49. *Guidelines for Air Quality Maintenance Planning and Analysis, Volume 9 (revised), Evaluating Indirect Sources*, EPA-450/4-78-001, September 1978.

50. M. A. Yocke, *et. al*, *Evalution of Short Term NO_2 Plume Models for Point Sources*, SAI Report 103-EF-80-91, EPA Contract No. 68-02-2775, (1980), in press.

10. ACKNOWLEDGEMENT

The principal authors of this document are Edwin L. Meyer, Jr., Donald H. Sennett, Henry S. Cole and Harold G. Richter. Valuable contributions have been made by David Iverach. The authors are also indebted to Carole J. Mask for her very able typing and clerical support.

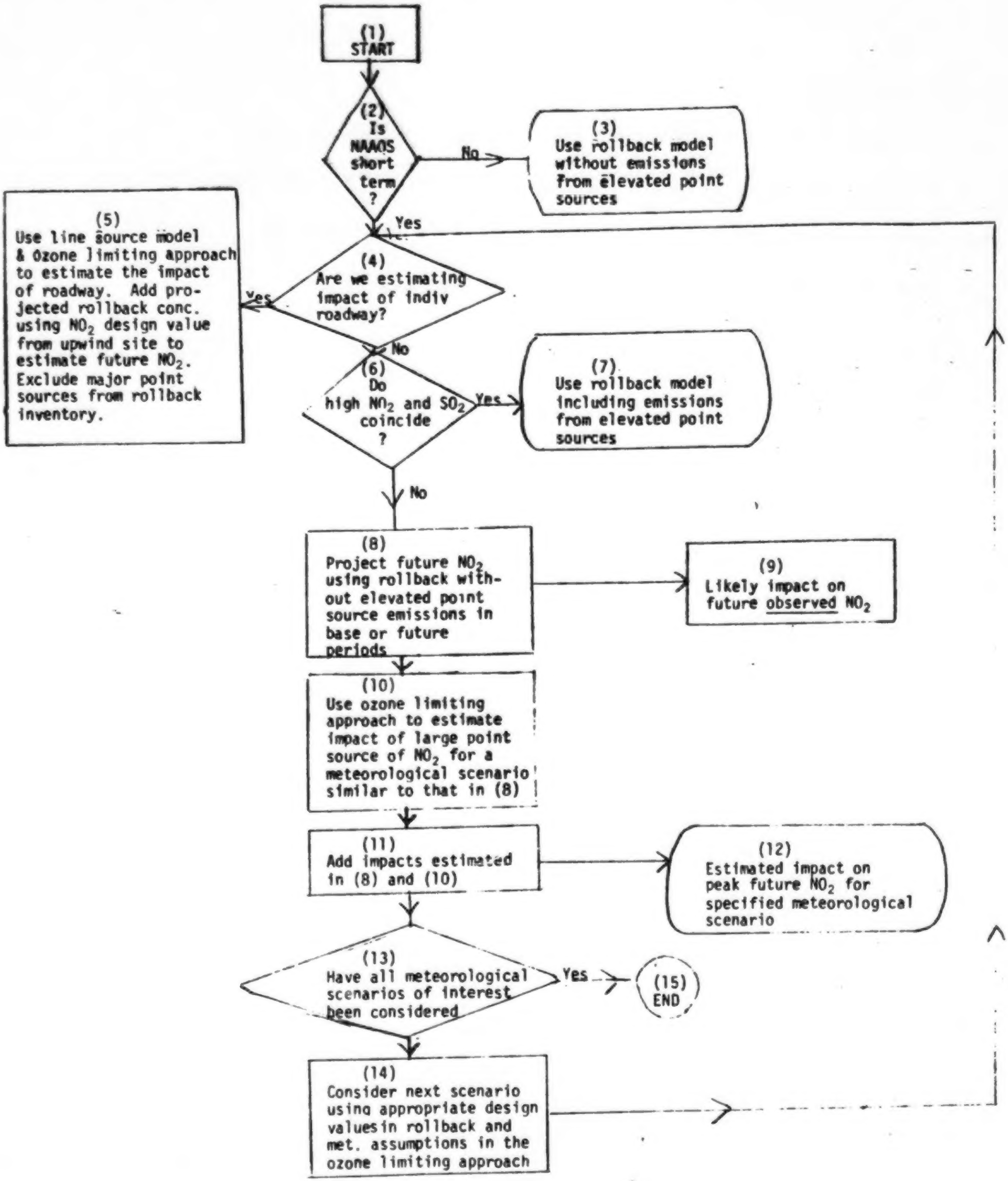

(1) START
(2) Is NAAQS short term ?
No
(3) Use rollback model without emissions from elevated point sources
Yes
(4) Are we estimating impact of indiv roadway?
Yes
(5) Use line source model & Ozone limiting approach to estimate the impact of roadway. Add projected rollback conc. using NO2 design value from upwind site to estimate future NO2. Exclude major point sources from rollback inventory.
No
(6) Do high NO2 and SO2 coincide ?
Yes
(7) Use rollback model including emissions from elevated point sources
No
(8) Project future NO2 using rollback without elevated point source emissions in base or future periods
(9) Likely impact on future observed NO2
(10) Use ozone limiting approach to estimate impact of large point source of NO2 for a meteorological scenario similar to that in (8)
(11) Add impacts estimated in (8) and (10)
(12) Estimated impact on peak future NO2 for specified meteorological scenario
(13) Have all meteorological scenarios of interest been considered
Yes
(15) END
(14) Consider next scenario using appropriate design valuesin rollback and met. assumptions in the ozone limiting approach

Figure 8.4 Modeling procedures for NO_2 SIP'S

TABLE 8.3 Approaches for Estimating Maximum Impact on Peak NO_2 from Large Individual Sources

Name	Description	Remarks
1) Partial Conversion	1) Multiply predicted maximum NO_x concentration by a constant factor to predict peak NO_2.	1) It is difficult to determine what the factor should be. Ambient measurements of NO_2/NO_x ratios within plumes vary widely. (See Fig. 7.6) Generally, the greater the dilution, the higher the ratio. As a rule, routinely collected monitoring data are not useful for these purposes, because they do not reflect the impact of point sources. Monitoring data collected in the vicinity ~200m of a major roadway may be of use for roadway applications.
2) Exponential Decay	2) Multiply predicted NO_x concentrations by an exponential decay factor $NO_2 = (rb)(NO_x)\ (1-e^{-.693t/T}) + (b)(NO_x)$ where t = travel time from source, time center T = half life conversion time of NO to NO_2, consistent units b = fraction of NO_x emitted as NO_2, assumed to be 0.10 for combustion sources, could be higher for industrial process sources. $(NO_x)_{max}$ = Maximum estimated ground level concentrations of NO_x using an inert pollutant model.	2) Conversion of NO to NO_2 appears to be limited by the oxidizing potential of the dilution air. Also, the half life of the NO is determined by dilution rather than chemistry. Any value chosen for the half life would have to be arbitrary.
3) Ozone Limiting Approach	3) Method assumes that maximum NO_2 concentration can be limited by dilution of an NO_x plume and/or the ozone concentrations in the dilution air. If ozone is the limiting factor, $[NO_2]_{max} = [O_3]_\tau = [NO_x]_{max}$ where $[O_3]_\tau$ = ambient ozone concentrations at the time peak NO_2 occurs. b = fraction of NO_x emitted as NO_2 $[NO_x]_{max}$ = Maximum ground level NO_x estimated with an inert point source model.	3) As discussed in Chapter 7.0, the summation of $(NO + NO_2 + O_3)$ appears to be constant across point source plumes (see Figures 7.9 and 7.10). This implies that NO to NO_2 conversion in plumes with high NO_x is limited by prevailing ambient ozone. Fewer arbitrary assumptions are required using this method than methods (1) or (2). Method assumes that complete mixing of the NO_x plumes occurrs at the point where maximum ground level NO occurs. It also ignores the likelihood of further photodisassociation of NO_2 upon formation. Measurements or estimates of prevailing ambient O_3 levels at the time $(NO_x)_{max}$ occurs are needed.
4) Photostationary State Approach	4) Approach combines $(NO_x)_{max}$ estimated with an inert pollutant model with the photostationary state relationship. As a result, $[NO_2]_{max}$ is estimated as follows: $[NO_2]_{max} = \frac{k_3\ [O_3]\ [NO_x]_{max}}{[k_1 +\ k_3[O_3]\ ]}$ where $[NO_x]_{max}$ = peak ground level NO_x concentrations estimated with a model for inert pollutants k_1 = the ratio constant in reaction with which NO_2 photodisassociates in the presence of sunlight: $NO_2 \xrightarrow[K_1]{h_\nu} NO + O$ k_3 = rate constant depicting the rate with which O_3 combines with NO to form NO_2: $NO + O_3 \xrightarrow[k_3]{} NO_2 + O_2$	4) White[26] and Cole et al.[43] have found this approach to work well in predicting maximum NO_2 downwind from a major point source and a major line source. The approach assumes thorough mixing of the plumes with ambient air at the point where $(NO_x)_{max}$ occurs. Measurements of the k_1 rate constant are not typically available. The approach also requires measurement of prevailing O_3 concentrations at the time $(NO_x)_{max}$ occurs.

TABLE B.3 Approaches for Estimating Maximum Impact on Peak NO_2 from Large Individual Sources

Name	Description	Remarks
1) Partial Conversion	1) Multiply predicted maximum NO_x concentration by a constant factor to predict peak NO_2.	1) It is difficult to determine what the factor should be. Ambient measurements of NO_2/NO_x ratios within plumes vary widely. (See Fig. 7.6) Generally, the greater the dilution, the higher the ratio. As a rule, routinely collected monitoring data are not useful for these purposes, because they do not reflect the impact of point sources. Monitoring data collected in the vicinity ~200m of a major roadway may be of use for roadway applications.
2) Exponential Decay	2) Multiply predicted NO_x concentrations by an exponential decay factor $NO_2 = (rb)(NO_x)\ (1-e^{.693\tau/\tau}) + (b)(NO_x)$ where t = travel time from source, time center T = half life conversion time of NO to NO_2, consistent units b = fraction of NO_x emitted as NO_2, assumed to be 0.10 for combustion sources, could be higher for industrial process sources. $(NO_x)_{max}$ = Maximum estimated ground level concentrations of NO_x using an inert pollutant model.	2) Conversion of NO to NO_2 appears to be limited by the oxidizing potential of the dilution air. Also, the half life of the NO is determined by dilution rather than chemistry. Any value chosen for the half life would have to be arbitrary.

TABLE 3.3 Approaches for Estimating Maximum Impact on Peak NO_2 from Large Individual Sources

Name	Description	Remarks
3) Ozone Limiting Approach	3) Method assumes that maximum NO_2 concentration can be limited by dilution of an NO_x plume and/or the ozone concentrations in the dilution air. If ozone is the limiting factor, $[NO_2]_{max} = [O_3]_\tau = [NO_x]_{max}$ where $[O_3]_\tau$ = ambient ozone concentrations at the time peak NO_2 occurs. b = fraction of NO_x emitted as NO_2 $[NO_x]_{max}$ = Maximum ground level NO_x estimated with an inert point source model.	3) As discussed in Chapter 7.0, the summation of $(NO + NO_2 + O_3)$ appears to be constant across point source plumes (see Figures 7.9 and 7.10). This implies that NO to NO_2 conversion in plumes with high NO_x is limited by prevailing ambient ozone. Fewer arbitrary assumptions are required using this method than methods (1) or (2). Method assumes that complete mixing of the NO_x plumes occurs at the point where maximum ground level NO occurs. It also ignores the likelihood of further photodisassociation of NO_2 upon formation. Measurements or estimates of prevailing ambient O_3 levels at the time $(NO_x)_{max}$ occurs are needed.
4) Photostationary State Approach	4) Approach combines $(NO_x)_{max}$ estimated with an inert pollutant model with the photostationary state relationship. As a result, $[NO_2]_{max}$ is estimated as follows: $[NO_2]_{max} = \frac{k_3\,[O_3]\,[NO_x]_{max}}{[k_1 + k_3[O_3]]}$ where $[NO_x]_{max}$ = peak ground level NO_x concentrations estimated with a model for inert pollutants k_1 = the ratio constant in reaction with which NO_2 photodisassociates in the presence of sunlight: $NO_2 \xrightarrow[K_1]{h\nu} NO + O$ k_3 = rate constant depicting the rate with which O_3 combines with NO to form NO_2: $NO + O_3 \xrightarrow[k_3]{} NO_2 + O_2$	4) White[26] and Cole et al.[43] have found this approach to work well in predicting maximum NO_2 downwind from a major point source and a major line source. The approach assumes thorough mixing of the plumes with ambient air at the point where $(NO_x)_{max}$ occurs. Measurements of the k_1 rate constant are not typically available. The approach also requires measurement of prevailing O_3 concentrations at the time $(NO_x)_{max}$ occurs.

TABLE 8.4 Hypothetical Example Illustrating Use of Multi- and Individual Source Models for Projecting Future Short-Term NO_2 Concentrations for Use in SIP's

Scenario	Time of Day	Estimated Peak Individual Source Contribution	Projected Multi-Source Contribution	Projected Peak NO_2
1) Observed nighttime-early morning peaks. Impact from elevated point source assumed to be negligible due to nocturnal inversion.	1900-0800	0	0.30 ppm	0.30 ppm
2) Observed mid-morning peaks. Multisource synthesis of NO_2 superimposed by fumigation impact from an elevated point source.	0900-1100	0.13 ppm	0.20 ppm	0.33 ppm
3) Observed mid-afternoon peaks. Potential point source impact is relatively high due to high observed O_3 levels at this time. Projected multisource impact is low due to low NO_2 concentrations observed by existing monitors during this time.	1200-1800	0.15 ppm	0.06 ppm	0.21 ppm